Supporting Information

Sulfoxide synthesis from sulfinate esters under Pummerer-like conditions

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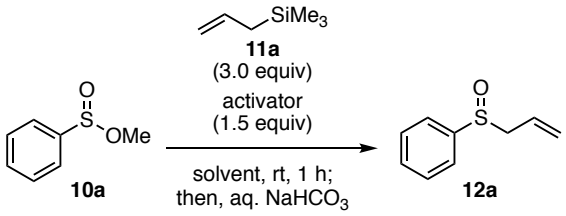
General Information

All reactions were performed with dry glassware under atmosphere of argon, unless otherwise noted. Analytical thin-layer chromatography (TLC) was performed on precoated (0.25 mm) silica-gel plates (Merck Chemicals, Silica Gel 60 F254, Cat. No. 1.05715. Column chromatography was conducted using silica-gel (Kanto Chemical Co., Inc., Silica Gel 60, spherical, particle size 40–50 μm, Cat. No. 37562-85). Melting points (Mp) were measured on an OptiMelt MPA100 (Stanford Research Systems), and are uncorrected. ^{1}H NMR spectra were obtained with a Bruker AVANCE 500 spectrometer at 500 MHz, or a Bruker AVANCE 400 spectrometer at 400 MHz. ^{13}C NMR spectra were obtained with a Bruker AVANCE 500 spectrometer at 126 MHz, or a Bruker AVANCE 400 spectrometer at 101 MHz. ^{19}F NMR spectra were obtained with a Bruker AVANCE 400 spectrometer at 376 MHz. All NMR measurements were carried out at 25 ºC. $CDCl_3$ (Kanto Chemical Co. Inc., Cat. No. 07663-23) was used as a solvent for obtaining NMR spectra. Chemical shifts (δ) are given in parts per million (ppm) downfield from $(CH_3)_4Si$ (δ 0.00 for ^{1}H NMR in $CDCl_3$) or the solvent peak (δ 77.0 for ^{13}C NMR in $CDCl_3$) as an internal reference or α,α,α-trifluorotoluene (δ –63.0 ppm for ^{19}F NMR in $CDCl_3$) as an external standard with coupling constants (*J*) in hertz (Hz). The abbreviations s, d, t, q, and m signify singlet, doublet, triplet, quartet, and multiplet, respectively. IR spectra were measured by diffuse reflectance method on a Shimadzu IRPrestige-21 spectrometer attached with DRS-8000A with the absorption band given in cm^{-1}. High-resolution mass spectra (HRMS) were measured on a Bruker micrOTOF mass spectrometer under positive electrospray ionization (ESI^{+}) conditions.

Methyl 4-toluenesulfinate (**10b**),[S1] methyl 4-methoxybenzenesulfinate (**10c**),[S1] methyl 4-chlorobenzenesulfinate (**10d**),[S2] methyl 4-nitrobenzenesulfinate (**10e**),[S3] methyl naphthalene-2-sulfinate (**10h**),[S2] methyl phenylmethanesulfinate (**10i**),[S2] methyl pentane-1-sulfinate (**10j**),[S4] and 4,4,5,5-tetramethyl-2-(3-((trimethylsilyl)methyl)prop-1-en-2-yl)-1,3,2-dioxaborolane[S5] were prepared according to the reported methods.

Optimization of Reaction Conditions

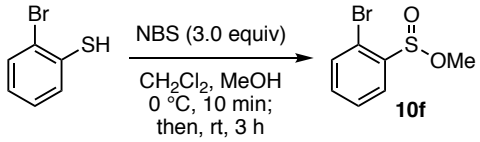


Entry	activator	solvent	Yield of **12a**[a]
1	Tf_2O	CH_2Cl_2	98% (89%)[b]
2	Ts_2O	CH_2Cl_2	0%
3	$(CF_3CO)_2O$	CH_2Cl_2	0%
4	Ac_2O	CH_2Cl_2	0%
5	$AlCl_3$	CH_2Cl_2	14%
6	$BF_3{\cdot}OEt_2$	CH_2Cl_2	0%
7	Me_3SiOTf	CH_2Cl_2	0%
8	TfOH	CH_2Cl_2	0%
9	Tf_2O	1,1,2,2-tetrachloroethane	95%
10	Tf_2O	CCl_4	60%
11	Tf_2O	$MeNO_2$	95%
12	Tf_2O	MeCN	54%
13[c]	Tf_2O	CH_2Cl_2	93%
14[d]	Tf_2O	CH_2Cl_2	65%
15[e]	Tf_2O	CH_2Cl_2	91%
16[f]	Tf_2O	CH_2Cl_2	86%

[a]Determined by ^1H NMR. [b]Isolated yield. [c]Tf_2O (1.0 equiv) was used. [d]Tf_2O (2.0 equiv) was used. [e]Allyltrimethylsilane (2.0 equiv) was used. [f]Allyltrimethylsilane (1.5 equiv) was used.

Experimental Procedures

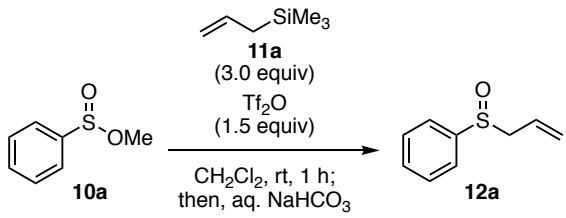
A typical procedure for the preparation of arylsulfinate esters[S2]



To a solution of 2-bromobenzenethiol (575 mg, 3.04 mmol) in dichloromethane (6.0 mL) and methanol (6.0 mL) was slowly added *N*-bromosuccinimide (1.07 g, 6.00 mmol, 2.0 equiv) at 0 ºC. After stirring for 10 min at the same temperature, the mixture was allowed to warm to room temperature. After stirring for 3 h at room temperature, to this were added an aqueous saturated solution of sodium bicarbonate (10 mL) and an aqueous saturated solution of sodium thiosulfate (10 mL). The mixture was extracted with dichloromethane (20 mL × 3), and the combined organic extract was washed with brine (10 mL), dried (Na_2SO_4), and after filtration, the filtrate was concentrated under reduced pressure. The residue was purified by flash column chromatography (silica-gel 13 g, *n*-hexane/EtOAc = 5/1) to give 2-bromobenzenesulfinate (**10f**) (582 mg, 2.47 mmol, 81%) as a colorless oil.

According to the procedure for preparing methyl 2-bromobenzenesulfinate (**10f**), methyl 2,6-dimethylbenzenesulfinate (**10g**) was prepared from 2,6-dimethylbenzenethiol.

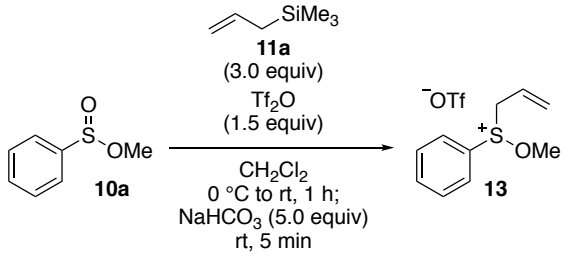
A typical procedure for the synthesis of allyl aryl sulfoxides from arylsulfinate esters with allyltrimethylsilanes



To a mixture of methyl benzenesulfinate (**10a**) (30.9 mg, 0.198 mmol) and allyltrimethylsilane (**11a**) (95.3 μL, 0.600 mmol, 3.0 equiv) in dichloromethane (2.0 mL) was added trifluoromethanesulfonic anhydride (50.4 μL, 0.300 mmol, 1.5 equiv) at room temperature. After stirring for 1 h at the same temperature, to the mixture was added an aqueous saturated solution of sodium bicarbonate (5 mL) and the mixture was extracted with dichloromethane (15 mL × 3). The combined organic extract was washed with brine (20 mL), dried (Na_2SO_4), and after filtration, the filtrate was concentrated under reduced pressure. The residue was purified by preparative TLC (*n*-hexane/EtOAc = 1/1) to give allyl phenyl sulfoxide (**12a**) (29.5 mg, 0.177 mmol, 89%) as a colorless oil.

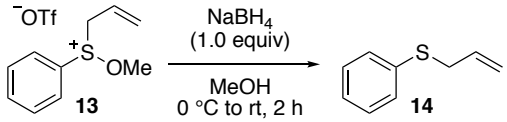
According to the procedure for preparing allyl phenyl sulfoxide (**12a**), allyl 4-tolyl sulfoxide (**12b**), allyl 4-methoxyphenyl sulfoxide (**12c**), allyl 4-chlorophenyl sulfoxide (**12d**), allyl 4-nitrophenyl sulfoxide (**12e**), allyl 2-bromophenyl sulfoxide (**12f**), allyl 2,6-dimethylphenyl sulfoxide (**12g**), allyl 2-naphthyl sulfoxide (**12h**), allyl benzyl sulfoxide (**12i**), allyl 1-pentyl sulfoxide (**12j**), 2-methylallyl phenyl sulfoxide (**12k**), phenyl 2-phenylallyl sulfoxide (**12l**), 2-(chloromethyl)allyl phenyl sulfoxide (**12m**), 2-(acetoxymethyl)allyl phenyl sulfoxide (**12n**), 2-(ethoxycarbonyl)allyl phenyl sulfoxide (**12o**), 2-bromoallyl phenyl sulfoxide (**12p**), phenyl 2-(trimethylsilyl)allyl sulfoxide (**12q**), phenyl 2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolyl)allyl sulfoxide (**12r**), 4-chlorophenyl 2-methylallyl sulfoxide (**12s**), and 2-bromoallyl 4-methoxyphenyl sulfoxide (**12t**) were prepared from the corresponding benzenesulfinate ester derivatives and allyltrimethylsilanes.

*Procedure for the synthesis of sulfonium salt **13** from arylsulfinate ester*



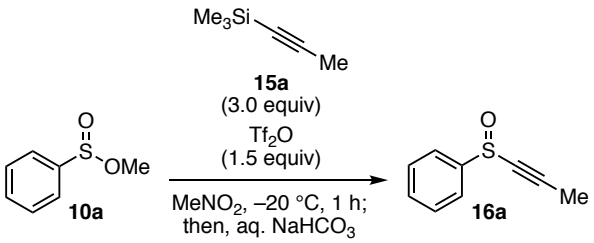
To a mixture of methyl benzenesulfinate (**10a**) (402 mg, 2.57 mmol) and allyltrimethylsilane (**11a**) (1.19 mL, 7.5 mmol, 3.0 equiv) in dichloromethane (25.0 mL) was added trifluoromethanesulfonic anhydride (50.4 μL, 0.300 mmol, 1.5 equiv) at 0 ºC. The mixture was allowed to warm to room temperature. After stirring for 1 h at room temperature, to the mixture was added sodium bicarbonate (1.05 g, 12.5 mmol, 5.0 equiv). After stirring for 5 min at the same temperature, the mixture was filtrated. The resulting filtrate was concentrated under reduced pressure. The resulting black oil was washed with Et_2O (5.0 mL × 3) and dried under reduced pressure to give allyl(methoxy)(phenyl)sulfonium trifluoromethanesulfonate (**13**) (863 mg, 2.57 mmol, quant.) as a black oil.

*Procedure for the synthesis of allyl aryl sulfide **14** from allyl aryl sulfonium*



To a mixture of allyl(methoxy)(phenyl)sulfonium trifluoromethanesulfonate (**13**) (66.6 mg, 0.202 mmol) in MeOH (2 mL) was added sodium borohydride (7.6 mg, 0.20 mmol, 1.0 equiv) at 0 ºC, the mixture was allowed to warm to room temperature. After stirring for 2 h at room temperature, to the mixture was added an aqueous saturated solution of ammonium chloride (5 mL) and the mixture was extracted with EtOAc (15 mL × 3). The combined organic extract was washed with brine (20 mL), dried (Na_2SO_4), and after filtration, the filtrate was concentrated under reduced pressure. To the residue was added 1,1,2,2-tetrachloroethane (18.8 mg, 0.106 mmol) as an internal standard, dissolved in $CDCl_3$, and ^1H NMR analysis (500 MHz) was performed. As a result, ^1H NMR yields of **14** was determined to be 80% by comparing the relative values of integration for the peaks observed at 5.14 ppm (1H for **14**) with that of 1,1,2,2-tetrachloroethane observed at 5.96 ppm. The volatile authentic sample was obtained as a colorless oil (9.9 mg, 0.66 mmol, 33%) by the purification with flash column chromatography (silica-gel 4.2 g, *n*-hexane/EtOAc = 50/1).

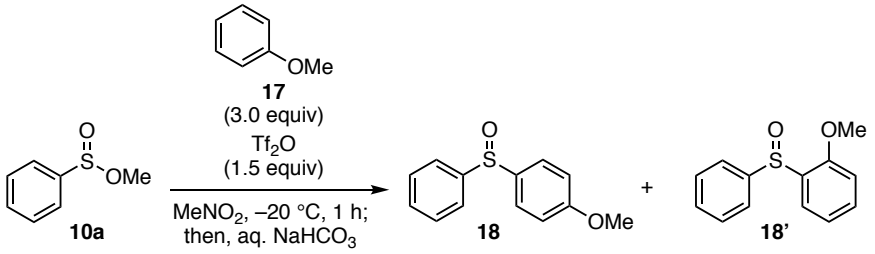
*A typical procedure for the synthesis of alkynyl aryl sulfoxides from benzenesulfinate ester **10a***



To a mixture of methyl benzenesulfinate (**10a**) (30.9 mg, 0.198 mmol) and 1-(trimethylsilyl)-1-propyne (**15a**) (88.6 μL, 0.600 mmol, 3.0 equiv) in nitromethane (2.0 mL) was added trifluoromethanesulfonic anhydride (50.4 μL, 0.300 mmol, 1.5 equiv) at –20 ºC. After stirring for 1 h at the same temperature, to the mixture was added an aqueous saturated solution of sodium bicarbonate (5 mL) and the mixture was extracted with dichloromethane (15 mL × 3). The combined organic extract was washed with brine (20 mL), dried (Na_2SO_4), and after filtration, the filtrate was concentrated under reduced pressure. The residue was purified by preparative TLC (*n*-hexane/EtOAc = 1/1) to give phenyl 1-propynyl sulfoxide (**16a**) (24.7 mg, 0.150 mmol, 75%) as a colorless oil.

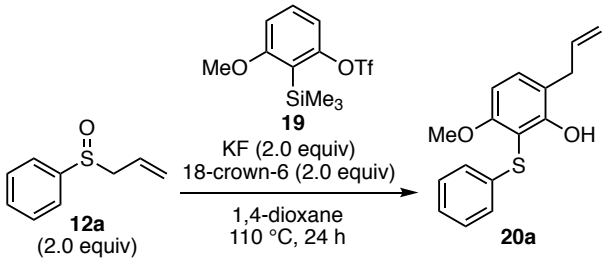
According to the procedure for preparing phenyl 1-propynyl sulfoxide (**16a**), phenyl phenylethynyl sulfoxide (**16b**) and (4-methoxyphenyl)ethynyl phenyl sulfoxide (**16c**) were prepared from (phenylethynyl)trimethylsilane (**15b**) and ((4-methoxyphenyl)ethynyl)trimethylsilane (**15c**), respectively.

*Procedure for the synthesis of diaryl sulfoxides from benzenesulfinate ester **10a***



To a mixture of methyl benzenesulfinate (**10a**) (30.6 mg, 0.196 mmol) and anisole (**17**) (64.9 mg, 0.600 mmol, 3.0 equiv) in nitromethane (200 μL) was added trifluoromethanesulfonic anhydride (50.4 μL, 0.300 mmol, 1.5 equiv) at –20 ºC. After stirring for 1 h at the same temperature, to the mixture was added an aqueous saturated solution of sodium bicarbonate (5 mL) and the mixture was extracted with dichloromethane (15 mL × 3). The combined organic extract was washed with brine (20 mL), dried (Na_2SO_4), and after filtration, the filtrate was concentrated under reduced pressure. The residue was purified by preparative TLC (*n*-hexane/EtOAc = 1/1) to give 4-methoxyphenyl phenyl sulfoxide (**18**) (32.5 mg, 0.140 mmol, 71%) as a colorless oil and 2-methoxyphenyl phenyl sulfoxide (**18'**) (4.3 mg, 19 μmol, 10%) as a colorless solid.

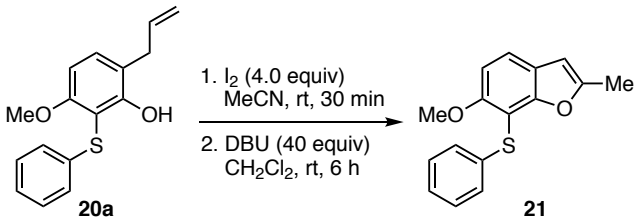
A typical procedure for the synthesis of highly functionalized phenols by direct oxythiolation of arynes with allyl aryl sulfoxides[S6]



To a mixture of 3-methoxy-2-(trimethylsilyl)phenyl triflate (**19**) (32.4 mg, 99.0 μmol) and allyl phenyl sulfoxide (**12a**) (33.2 mg, 0.200 mmol, 2.0 equiv) in 1,4-dioxane (2.0 mL) were added 18-crown-6-ether (52.9 mg, 0.200 mmol, 2.0 equiv) and potassium fluoride (11.6 mg, 0.200 mmol, 2.0 equiv) at room temperature. After stirring for 24 h at 110 ºC, the mixture was cooled to room temperature, and to this was added water (5 mL). The mixture was extracted with EtOAc (15 mL × 3), and the combined organic extract was washed with brine (20 mL), dried (Na_2SO_4), and after filtration, the filtrate was concentrated under reduced pressure. The residue was purified by preparative TLC (*n*-hexane/CH_2Cl_2 = 1/1) to give 6-allyl-3-methoxy-2-(phenylthio)phenol (**20a**) (13.9 mg, 51.0 μmol, 52%) as a colorless oil.

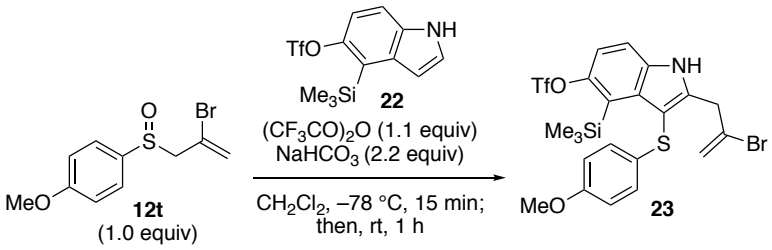
According to the procedure for preparing 6-allyl-3-methoxy-2-(phenylthio)phenol (**20a**), using 4-chlorophenyl 2-methylallyl sulfoxide (**12s**) instead of allyl phenyl sulfoxide (**12a**), 2-((4-chlorophenyl)thio)-3-methoxy-6-(2-methylallyl)phenol (**20b**) was prepared.

*Intramolecular cyclization for the synthesis of multisubstituted benzofuran **21***[S7]



To a solution of 6-allyl-3-methoxy-2-(phenylthio)phenol (**20a**) (27.2 mg, 0.100 mmol) in MeCN (4.0 mL) was added I_2 (90.8 mg, 0.400 mmol, 4.0 equiv) at room temperature. After stirring for 30 min at the same temperature, to the mixture was added dichloromethane (20 mL), followed by the addition of DBU (600 μL, 4.01 mmol, 40 equiv). After stirring for 6 h at the same temperature, to the mixture was added brine (5 mL) and the mixture was extracted with dichloromethane (15 mL × 3). The combined organic extract was dried (Na_2SO_4), and after filtration, the filtrate was concentrated under reduced pressure. The residue was purified by preparative TLC (*n*-hexane/EtOAc = 20/1) to give 6-methoxy-2-methyl-7-(phenylthio)benzo[*b*]furan (**21**) (11.4 mg, 42.0 μmol, 42%) as a colorless oil.

*Synthesis of tetrasubstituted indole **23** via an interrupted Pummerer coupling/[3,3]-sigmatropic rearrangement*[S8]

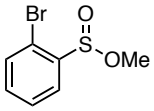


To a mixture 2-bromoallyl 4-methoxyphenyl sulfoxide (**12t**) (29.3 mg, 0.106 mmol, 1.0 equiv), 5-triflyloxy-4-(trimethylsilyl)-1*H*-indole (**22**) (34.1 mg, 0.101 mmol) and sodium bicarbonate (18.5 mg, 0.220 mmol, 2.2 equiv) in dichloromethane (1.0 mL) was added trifluoroacetic anhydride (23.1 mg, 0.110 mmol, 1.1 equiv) at –78 ºC. After stirring for 15 min at the same temperature, the mixture was allowed to warm to room temperature. After stirring for 1 h at room temperature, the crude reaction mixture was filtered through a plug of silica, eluted with dichloromethane (20 mL), and concentrated under reduced pressure. The residue was purified by preparative TLC (*n*-hexane/CH_2Cl_2 = 1/1) to give 2-(2-bromoallyl)-3-((4-methoxyphenyl)thio)-5-triflyloxy-4-trimethylsilyl-1*H*-indole (**23**) (53.1 mg, 89.0 μmol, 84%) as a pale yellow oil.

Characterization Data of New Compounds

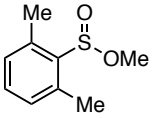
Allyl phenyl sulfoxide (**12a**),[S6] allyl 4-tolyl sulfoxide (**12b**),[S6] allyl 4-methoxyphenyl sulfoxide (**12c**),[S6] allyl 4-chlorophenyl sulfoxide (**12d**),[S6] allyl 4-nitrophenyl sulfoxide (**12e**),[S9] allyl 2-bromophenyl sulfoxide (**12f**),[S6] allyl 2,6-dimethylphenyl sulfoxide (**12g**),[S6] allyl 2-naphthyl sulfoxide (**12h**),[S10] allyl benzyl sulfoxide (**12i**),[S11] 2-methylallyl phenyl sulfoxide (**12k**),[S9] phenyl 2-phenylallyl sulfoxide (**12l**),[S9] 2-bromoallyl phenyl sulfoxide (**12p**),[S9] allyl phenyl sulfide (**14**),[S12] phenyl 1-propynyl sulfoxide (**16a**),[S13] phenyl phenylethynyl sulfoxide (**16b**),[S14] (4-methoxyphenyl)ethynyl phenyl sulfoxide (**16c**),[S15] 4-methoxyphenyl phenyl sulfoxide (**18**),[S16] and 2-methoxyphenyl phenyl sulfoxide (**18'**)[S16] were identical in spectra data with those reported in the literature.

Methyl 2-bromobenzenesulfinate (**10f**)



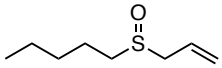
Yield: 81% (582 mg, 2.47 mmol); Colorless oil; TLC R_f 0.33 (*n*-hexane/EtOAc = 5/1); ^{1}H NMR ($CDCl_3$, 500 MHz): δ 3.60 (s, 3H), 7.42 (ddd, 1H, J = 7.7, 7.7, 1.7 Hz), 7.53 (ddd, 1H, J = 7.7, 7.7, 0.9 Hz), 7.62 (dd, 1H, J = 7.7, 0.9 Hz), 7.93 (dd, 1H, J = 7.7, 1.7 Hz); ^{13}C{^{1}H} NMR ($CDCl_3$, 126 MHz): δ 51.5, 121.1, 127.0, 127.7, 133.56, 133.61, 142.7; IR (KBr, cm^{-1}) 685, 708, 718, 760, 966, 1020, 1125, 1132, 1447; HRMS (ESI) *m/z*: $[M + H]^+$ Calcd for $C_7H_7{}^{79}BrNaO_2S^+$ 256.9242; Found 256.9235.

Methyl 2,6-dimethylbenzenesulfinate (**10g**)



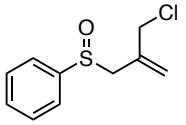
Yield: 94% (176 mg, 0.955 mmol); Colorless oil; TLC R_f 0.34 (*n*-hexane/EtOAc = 5/1); ^{1}H NMR ($CDCl_3$, 500 MHz): δ 2.62 (s, 6H), 3.82 (s, 3H), 7.04 (d, 2H, J = 7.6 Hz), 7.24 (t, 1H, J = 7.6 Hz); ^{13}C{^{1}H} NMR ($CDCl_3$, 126 MHz): δ 19.1, 54.6, 130.0, 131.6, 137.8, 140.6; IR (KBr, cm^{-1}) 596, 694, 723, 777, 986, 1117, 1132, 1460, 2934; HRMS (ESI) *m/z*: $[M + H]^+$ Calcd for $C_9H_{13}O_2S^+$ 185.0631; Found 185.0634.

Allyl 1-pentyl sulfoxide (**12j**)



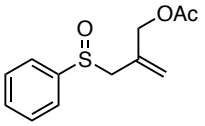
Yield: 88% (28.2 mg, 0.176 mmol); Colorless oil; TLC R_f 0.22 (EtOAc); ^{1}H NMR ($CDCl_3$, 500 MHz): δ 0.91 (t, 3H, J = 7.2 Hz), 1.33–1.49 (m, 4H), 1.71–1.80 (m, 2H), 2.63–2.72 (m, 2H), 3.41 (dd, 1H, J = 13.0, 7.5 Hz), 3.49 (dd, 1H, J = 13.0, 7.5 Hz), 5.36–5.44 (m, 2H), 5.89 (dddd, 1H, J = 17.2, 10.2, 7.5, 7.5 Hz); ^{13}C{^{1}H} NMR ($CDCl_3$, 126 MHz): 13.8, 22.1, 22.3, 31.0, 51.0, 55.8, 123.3, 125.9; IR (KBr, cm^{-1}) 581, 926, 1030, 1458, 1464, 2860, 2930, 2957; HRMS (ESI) *m/z*:g $[M + H]^+$ Calcd for $C_8H_{17}OS^+$ 161.0995; Found 161.0997.

2-(Chloromethyl)allyl phenyl sulfoxide (**12m**)



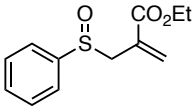
Yield: 76% (32.8 mg, 0.150 mmol); Colorless solid; Mp 34–36 °C; TLC R_f 0.31 (*n*-hexane/EtOAc = 1/1); ^{1}H NMR ($CDCl_3$, 500 MHz): δ 3.56 (d, 1H, J = 13.2 Hz), 3.68 (d, 1H, J = 13.2 Hz), 3.94 (d, 1H, J = 12.0 Hz), 4.09 (d, 1H, J = 12.0 Hz), 5.08 (s, 1H), 5.41 (s, 1H), 7.50–7.55 (m, 3H), 7.61–7.64 (AA'BB'C, 2H); ^{13}C{^{1}H} NMR ($CDCl_3$, 126 MHz): δ 47.7, 61.0, 122.4, 124.1, 129.2, 131.3, 134.7, 143.2; IR (KBr, cm^{-1}) 557, 692, 748, 920, 1020, 1042,1086, 1420, 1443; HRMS (ESI) *m/z*: $[M + H]^+$ Calcd for $C_{10}H_{11}{}^{35}ClNaOS^+$ 237.0111; Found 237.0110.

2-(Acetoxymethyl)allyl phenyl sulfoxide (**12n**)



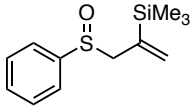
Yield: 80% (38.8 mg, 0.163 mmol); Colorless oil; TLC R_f 0.15 (*n*-hexane/EtOAc = 1/1); ^{1}H NMR ($CDCl_3$, 500 MHz): δ 2.08 (s, 3H), 3.51–3.57 (m, 2H), 4.46 (d, 1H, *J* = 10.6 Hz), 4.54 (d, 1H, *J* = 10.6 Hz), 5.05 (s, 1H), 5.33 (s, 1H), 7.51–7.54 (m, 3H), 7.61–7.63 (AA'BB'C, 2H); ^{13}C{^{1}H} NMR ($CDCl_3$, 126 MHz): δ 20.9, 61.9, 66.4, 121.4, 124.2, 129.1, 131.3, 133.4, 143.4, 170.5; IR (KBr, cm^{-1}) 750, 918, 1042, 1231, 1375, 1422, 1445, 1740; HRMS (ESI) *m/z*: [M + H]$^+$ Calcd for $C_{12}H_{14}NaO_3S^+$ 261.0556; Found 261.0558.

2-(Ethoxycarbonyl)allyl phenyl sulfoxide (**12o**)



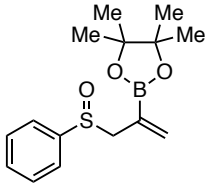
Yield: 31% (15.9 mg, 67.0 μmol); Colorless oil; TLC R_f 0.23 (*n*-hexane/EtOAc = 1/1); ^{1}H NMR ($CDCl_3$, 500 MHz): δ 1.24 (t, 3H, *J* = 7.2 Hz), 3.73 (d, 1H, *J* = 12.6 Hz), 3.80 (dd, 1H, *J* = 12.6, 0.8 Hz), 4.07–4.13 (m, 2H), 5.77 (d, 1H, *J* = 0.8 Hz), 6.44 (d, 1H, *J* = 0.8 Hz), 7.48–7.52 (m, 3H), 7.59–7.62 (AA'BB'C, 2H); ^{13}C{^{1}H} NMR ($CDCl_3$, 126 MHz): δ 14.1, 59.4, 61.3, 124.3, 129.0, 129.3, 131.2, 132.1, 143.0, 165.4; IR (KBr, cm^{-1}) 752, 1043, 1190, 1327, 1371, 1420, 1445, 1745; HRMS (ESI) *m/z*: [M + H]$^+$ Calcd for $C_{12}H_{14}NaO_3S^+$ 261.0556; Found 261.0552.

Phenyl 2-(trimethylsilyl)allyl sulfoxide (**12q**)



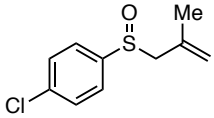
Yield: 46% (23.7 mg, 99.0 μmol); Pale yellow oil; TLC R_f 0.42 (*n*-hexane/EtOAc = 1/1); ^{1}H NMR ($CDCl_3$, 500 MHz): δ 0.13 (s, 9H), 3.53 (dd, 1H, *J* = 12.5, 0.8 Hz), 3.68 (d, 1H, *J* = 12.5 Hz), 5.63 (d, 1H, *J* = 2.2 Hz), 5.68–5.69 (m, 1H), 7.47–7.53 (m, 3H), 7.61–7.63 (AA'BB'C, 2H); ^{13}C{^{1}H} NMR ($CDCl_3$, 126 MHz): δ –1.6, 65.4, 124.5, 129.0, 131.1, 133.3, 140.9, 144.0; IR (KBr, cm^{-1}) 918, 1040, 1375, 1422, 1443; HRMS (ESI) *m/z*: [M + H]$^+$ Calcd for $C_{12}H_{18}NaOSSi^+$ 261.0740; Found 261.0733.

Phenyl 2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolyl)allyl sulfoxide (**12r**)



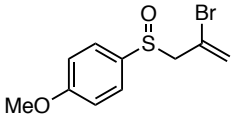
Yield: 76% (45.2 mg, 0.155 mmol); Colorless solid; Mp 68–70 °C; TLC R_f 0.24 (*n*-hexane/EtOAc = 1/1); ^{1}H NMR ($CDCl_3$, 500 MHz): δ 1.17 (s, 6H), 1.18 (s, 6H), 3.63–3.68 (m, 2H), 5.71 (d, 1H, *J* = 2.4 Hz), 6.08 (d, 1H *J* = 2.4 Hz), 7.44–7.50 (m, 3H), 7.57–7.60 (AA'BB'C, 2H); ^{13}C{^{1}H} NMR ($CDCl_3$, 126 MHz): δ 24.7, 24.8, 62.1, 84.0, 124.8, 128.8, 130.8, 137.5, 143.3 (the signal for the carbon which is attached to the boron atom was not observed); IR (KBr, cm^{-1}) 918, 1040, 1375, 1422, 1443; HRMS (ESI) *m/z*: [M + H]$^+$ Calcd for $C_{15}H_{21}BNaO_3S^+$ 315.1197; Found 315.1209.

4-Chlorophenyl 2-methylallyl sulfoxide (**12s**)



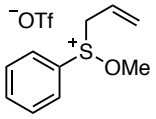
Yield: 80% (172 mg, 0.802 mmol); Colorless solid; Mp 33–35 °C; TLC R_f 0.36 (*n*-hexane/EtOAc = 1/1); ^{1}H NMR ($CDCl_3$, 400 MHz): δ 1.80–1.81 (m, 3H), 3.37 (dd, 1H, *J* = 12.4, 0.7 Hz), 3.52 (dd, 1H, *J* = 12.4, 0.7 Hz), 4.78 (s, 1H), 5.02–5.03 (m, 1H), 7.46–7.50 (AA'BB', 2H), 7.54–7.57 (AA'BB', 2H); ^{13}C{^{1}H} NMR ($CDCl_3$, 101 MHz): δ 22.9, 66.7, 119.0, 125.6, 129.3, 134.5, 137.3, 142.4; IR (KBr, cm^{-1}) 741, 816, 905, 1011, 1049, 1090, 1391, 1476; HRMS (ESI) *m/z*: [M + H]$^+$ Calcd for $C_{10}H_{11}{}^{35}ClNaOS^+$ 237.0111; Found 237.0113.

2-Bromoallyl 4-methoxyphenyl sulfoxide (**12t**)



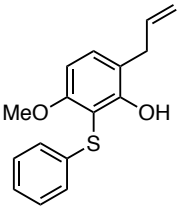
Yield: 53% (152 mg, 0.550 mmol); Colorless oil; TLC R_f 0.22 (*n*-hexane/EtOAc = 1/1); ^{1}H NMR ($CDCl_3$, 500 MHz): δ 3.68 (d, 1H, *J* = 13.1 Hz), 3.86 (s, 3H), 3.93 (d, 1H, *J* = 13.1 Hz), 5.64 (s, 1H), 5.68 (s, 1H), 7.03 (d, 2H, *J* = 8.7 Hz), 7.60 (d, 2H, *J* = 8.7 Hz); ^{13}C{^{1}H} NMR ($CDCl_3$, 126 MHz): δ 55.5, 69.9, 114.7, 120.4, 124.0, 126.3, 133.6, 162.3; IR (KBr, cm^{-1}) 831, 1028, 1045, 1086, 1254, 1304, 1497, 1593; HRMS (ESI) *m/z*: $[M + H]^+$ Calcd for $C_{10}H_{11}{}^{79}BrNaO_2S^+$ 296.9555; Found 296.9533.

Allyl(methoxy)(phenyl)sulfonium trifluoromethanesulfonate (**13**)



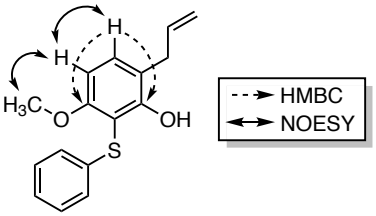
Yield: quant. (863.1 mg, 2.57 mmol); Black oil; ^{1}H NMR ($CDCl_3$, 500 MHz): δ 4.11 (s, 3H), 4.56–4.65 (m, 2H), 5.58 (d, 1H, *J* = 3.5 Hz), 5.61 (d, 1H, *J* = 3.5 Hz), 5.76–5.82 (m, 1H), 7.71–7.75 (AA'BB'C, 2H), 7.81–7.85 (AA'BB'C, 1H), 7.98–8.01 (AA'BB'C, 2H); ^{13}C{^{1}H} NMR ($CDCl_3$, 126 MHz): δ 55.2, 64.1, 120.3 (q, $^1J_{C–F}$ = 319.7 Hz), 121.0, 126.6, 129.4, 130.1, 130.9, 136.5; ^{19}F NMR ($CDCl_3$, 376 MHz): δ −78.7 (s); IR (KBr, cm^{-1}) 577, 642, 752, 1034, 1167, 1229, 1261, 1670; HRMS (ESI) *m/z*: $[M – OTf]^+$ Calcd for $C_{10}H_{13}OS^+$ 181.0682; Found 181.0678.

6-Allyl-3-methoxy-2-(phenylthio)phenol (**20a**)

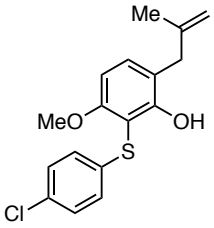


Yield: 52% (13.9 mg, 51.0 μmol); Colorless oil; TLC R_f 0.31 (*n*-hexane/CH_2Cl_2 = 3/1); ^{1}H NMR ($CDCl_3$, 500 MHz): δ 3.47–3.48 (m, 2H), 3.86 (s, 3H), 4.96–5.04 (m, 2H), 5.95–6.03 (m, 1H), 6.55 (d, 1H, *J* = 8.6 Hz), 6.63 (s, 1H), 7.03–7.05 (AA'BB'C, 2H), 7.11–7.14 (AA'BB'C, 1H), 7.20–7.24 (AA'BB'C, 2H), 7.41 (d, 1H, *J* = 8.6 Hz); ^{13}C{^{1}H} NMR ($CDCl_3$, 126 MHz): δ 28.0, 55.8, 103.9, 107.6, 114.4, 114.7, 125.7, 126.2, 129.1, 135.3, 136.0, 136.9, 156.0, 160.5; IR (KBr, cm^{-1}) 739, 793, 1070, 1088, 1115, 1225, 1275, 1323, 1439, 1462, 1483, 1582, 1601, 3418; HRMS (ESI) *m/z*: $[M + H]^+$ Calcd for $C_{16}H_{16}NaO_2S^+$ 295.0763; Found 295.0761.

The regiochemistry of **20a** was determined by the HMBC and the NOESY experiments.

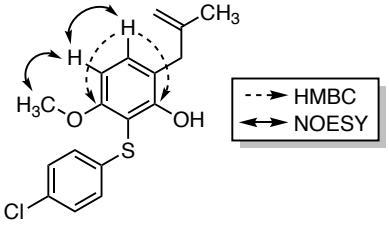


2-((4-Chlorophenyl)thio)-3-methoxy-6-(2-methylallyl)phenol (**20b**)

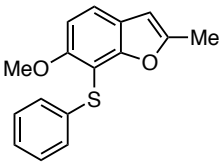


Yield: 32% (10.7 mg, 33.0 μmol); Colorless oil; TLC R_f 0.38 (*n*-hexane/CH_2Cl_2 = 3/1); ^{1}H NMR ($CDCl_3$, 500 MHz): δ 1.79 (s, 3H), 3.41 (s, 2H), 3.85 (s, 3H), 4.50 (s, 1H), 4.71–4.72 (m, 1H), 6.52 (s, 1H), 6.56 (d, 1H, *J* = 8.6 Hz), 6.93–6.96 (AA'BB', 2H), 7.16–7.19 (AA'BB', 2H), 7.39 (d, 1H, *J* = 8.6 Hz); ^{13}C{^{1}H} NMR ($CDCl_3$, 126 MHz): δ 22.9, 31.6, 55.8, 104.1, 107.2, 109.6, 115.0, 127.4, 129.2, 131.7, 135.3, 135.6, 144.2, 156.1, 161.0; IR (KBr, cm^{-1}) 918, 1038, 1090, 1375, 1422, 1435, 1476, 2943, 3624; HRMS (ESI) *m/z*: [M + H]$^+$ Calcd for $C_{17}H_{17}{}^{35}ClNaO_2S^+$ 343.0530; Found 343.0521.

The regiochemistry of **20b** was determined by the HMBC and the NOESY experiments.

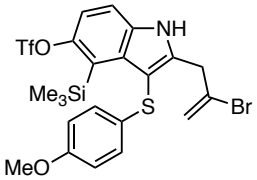


6-Methoxy-2-methyl-7-(phenylthio)benzo[*b*]furan (**21**)



Yield: 42% (11.4 mg, 42.0 μmol); Colorless oil; TLC R_f 0.29 (*n*-hexane/CH_2Cl_2 = 3/1); ^{1}H NMR ($CDCl_3$, 500 MHz): δ 2.42 (d, 3H, *J* = 1.1 Hz), 3.95 (s, 3H), 6.50 (q, 1H, *J* = 1.1 Hz), 6.66 (d, 1H, *J* = 8.3 Hz), 7.10–7.15 (m, 3H), 7.18–7.21 (AA'BB'C, 2H), 7.31 (d, 1H, *J* = 8.3 Hz); ^{13}C{^{1}H} NMR ($CDCl_3$, 126 MHz): δ 14.1, 55.7, 100.5, 104.3, 106.4, 119.7, 125.5, 127.4, 128.8, 131.2, 137.7, 154.0, 154.8, 156.1; IR (KBr, cm^{-1}) 739, 797, 1086, 1146, 1217, 1279, 1439, 1477, 1493, 1587; HRMS (ESI) *m/z*: [M + H]$^+$ Calcd for $C_{16}H_{14}NaO_2S^+$ 293.0607; Found 293.0608.

2-(2-Bromoallyl)-3-((4-methoxyphenyl)thio)-5-triflyloxy-4-(trimethylsilyl)-1*H*-indole (**23**)



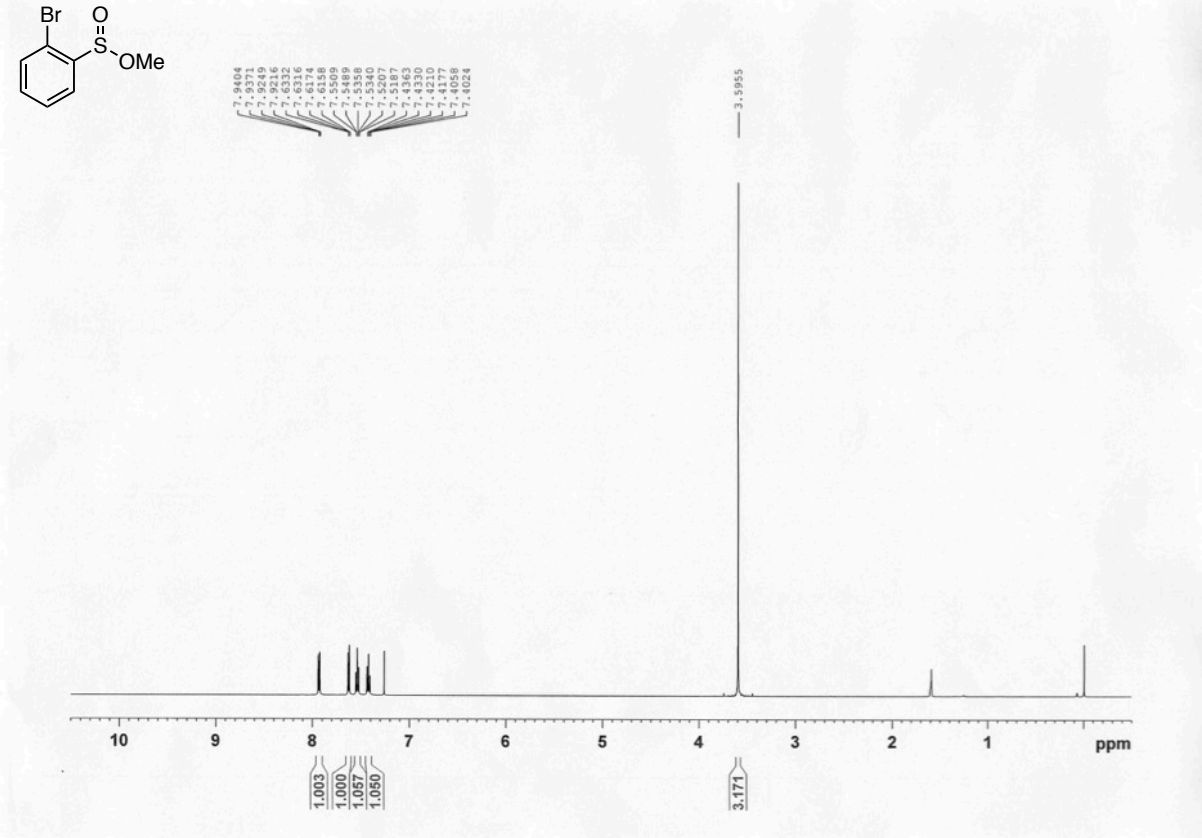
Yield: 84% (53.1 mg, 89.0 μmol); Pale yellow oil; TLC R_f 0.30 (*n*-hexane/CH_2Cl_2 = 1/1); ^{1}H NMR ($CDCl_3$, 500 MHz): δ 0.48 (s, 9H), 3.72 (s, 3H), 4.02 (s, 2H), 5.51–5.52 (m, 1H), 5.55–5.57 (m, 1H), 6.67–6.70 (AA'BB', 2H), 6.74–6.77 (AA'BB', 2H), 7.14 (d, 1H, *J* = 8.8 Hz), 7.43 (d, 1H, *J* = 8.8 Hz), 8.72 (s, 1H); ^{13}C{^{1}H} NMR ($CDCl_3$, 126 MHz): δ 3.0, 38.9, 55.3, 104.8, 113.6, 114.6, 116.1, 118.7 (q, J_{C-F} = 320.8 Hz), 120.6, 125.6, 127.2, 127.6, 130.3, 133.5, 135.2, 142.7, 149.8, 157.5; ^{19}F NMR ($CDCl_3$, 376 MHz): δ −72.9 (s); IR (KBr, cm^{-1}) 845, 878, 984, 1130, 1144, 1211, 1246, 1391, 1412, 1493; HRMS (ESI) *m/z*: [M + H]$^+$ Calcd for $C_{22}H_{23}{}^{79}BrF_3NNaO_4S_2Si^+$ 615.9865; Found 615.9853.

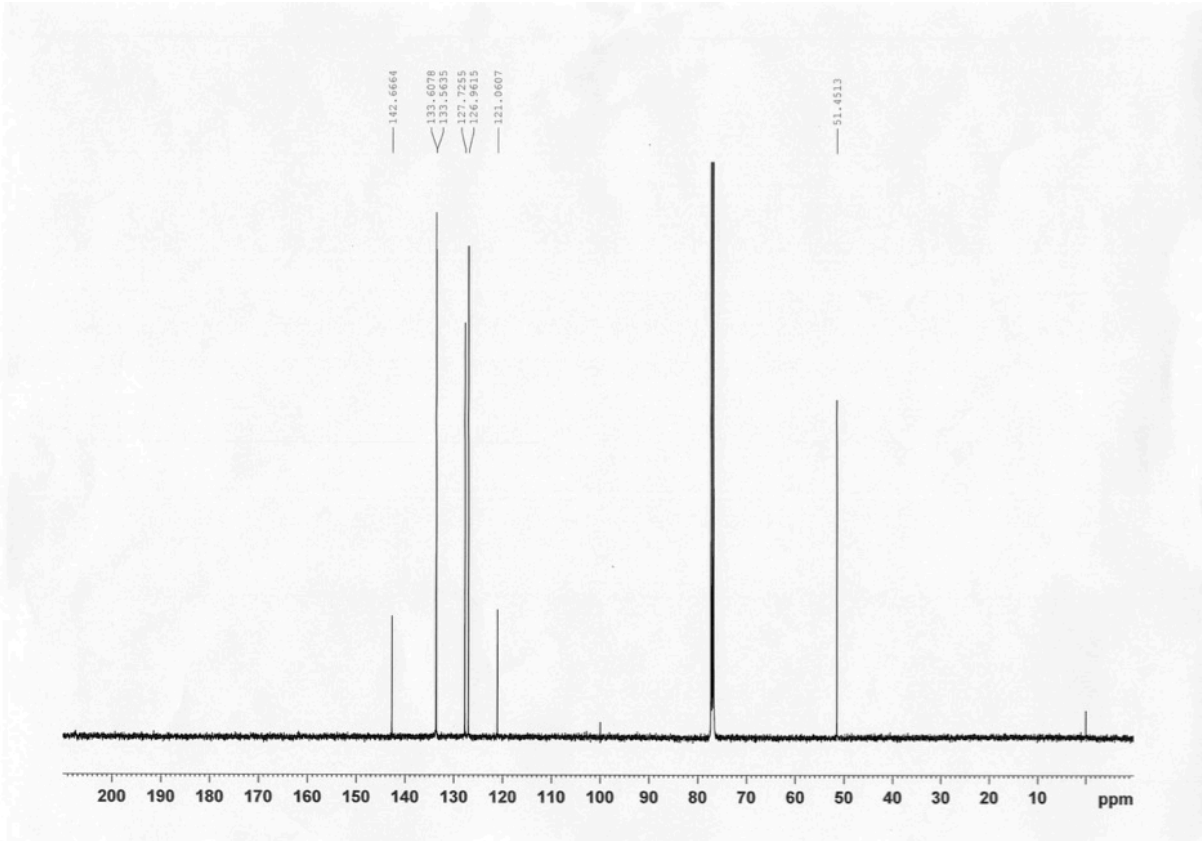
References for Supporting Information

S1 R. Ma and M. C. White, *J. Am. Chem. Soc.*, 2018, **140**, 3202.
S2 J. A. Lujan-Montelongo, A. O. Estevez and F. F. Fleming, *Eur. J. Org. Chem.*, **2015**, 1602.
S3 J. L. Garcia Ruano, J. Alemán, C. Fajardo and A. Parra, *Org. Lett.*, 2005, **7**, 5493.
S4 T. L. Moore and D. E. O'Connor, *J. Org. Chem.*, 1966, **31**, 3587.
S5 S. M. Marcuccio and H. Weigold, WO 2001/029051 A1, 2001.
S6 Y. Li, D. Qiu, R. Gu, J. Wang, J. Shi and Y. Li, *J. Am. Chem. Soc.,* 2016, **138**, 14582.
S7 A. K. Yadav, B. K. Singh, N. Singh and R. P. Tripathi, *Tetrahedron Lett.*, 2007, **48**, 6628.
S8 M. Šiaučiulis, S. Sapmaz, A. P. Pulis and D. J. Procter, *Chem. Sci.*, 2018, **9**, 754.
S9 V. Pace, L. Castoldi and W. Holzer, *Tetrahedron Lett.*, 2012, **53**, 967.
S10 G. Maitro, G. Prestat, D. Madec and G. Poli, *J. Org. Chem.*, 2006, **71**, 7449.
S11 M. Turks, A. K. Lawrence and P. Vogel, *Tetrahedron Lett.*, 2006, **53**, 967.
S12 V. Pace, L. Castoldi and W. Holzer, *Tetrahedron Lett.*, 2012, **47**, 2783.
S13 J. P. Marino and H. N. Nguyen, *J. Org. Chem.*, 2002, **67**, 6291.
S14 J. Wei and Z. Sun, *Org. Lett.*, 2015, **17**, 5396.
S15 B. Alcaide, P. Almendros and C. Lázaro-Milla, *Adv. Synth. Catal.*, 2017, **359**, 2630.
S16 H. Yu, Z. Li and C. Bolm, *Org. Lett.*, 2018, **20**, 7104.

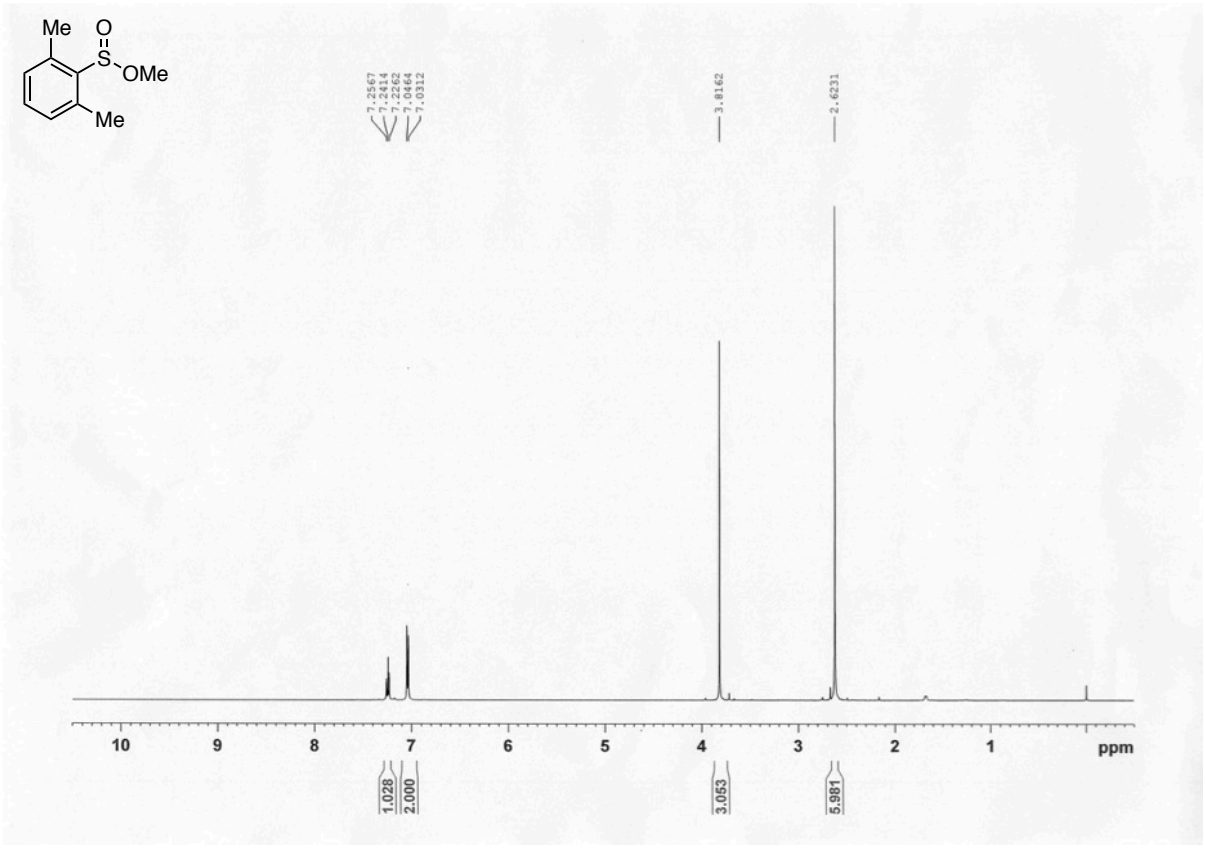
^{1}H and ^{13}C NMR Spectra of Compounds

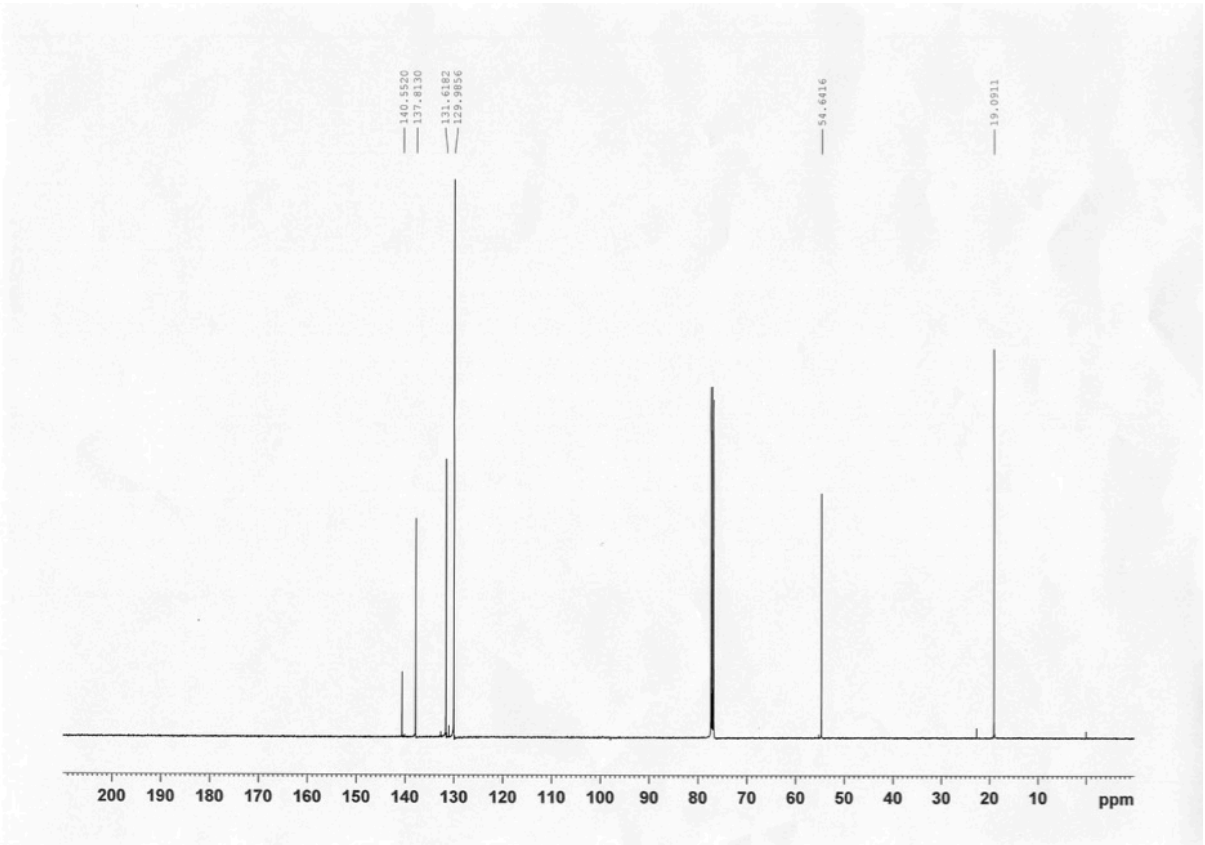
^{1}H NMR (500 MHz) and ^{13}C NMR (126 MHz) spectra of methyl 2-bromobenzenesulfinate (**10f**) ($CDCl_3$)



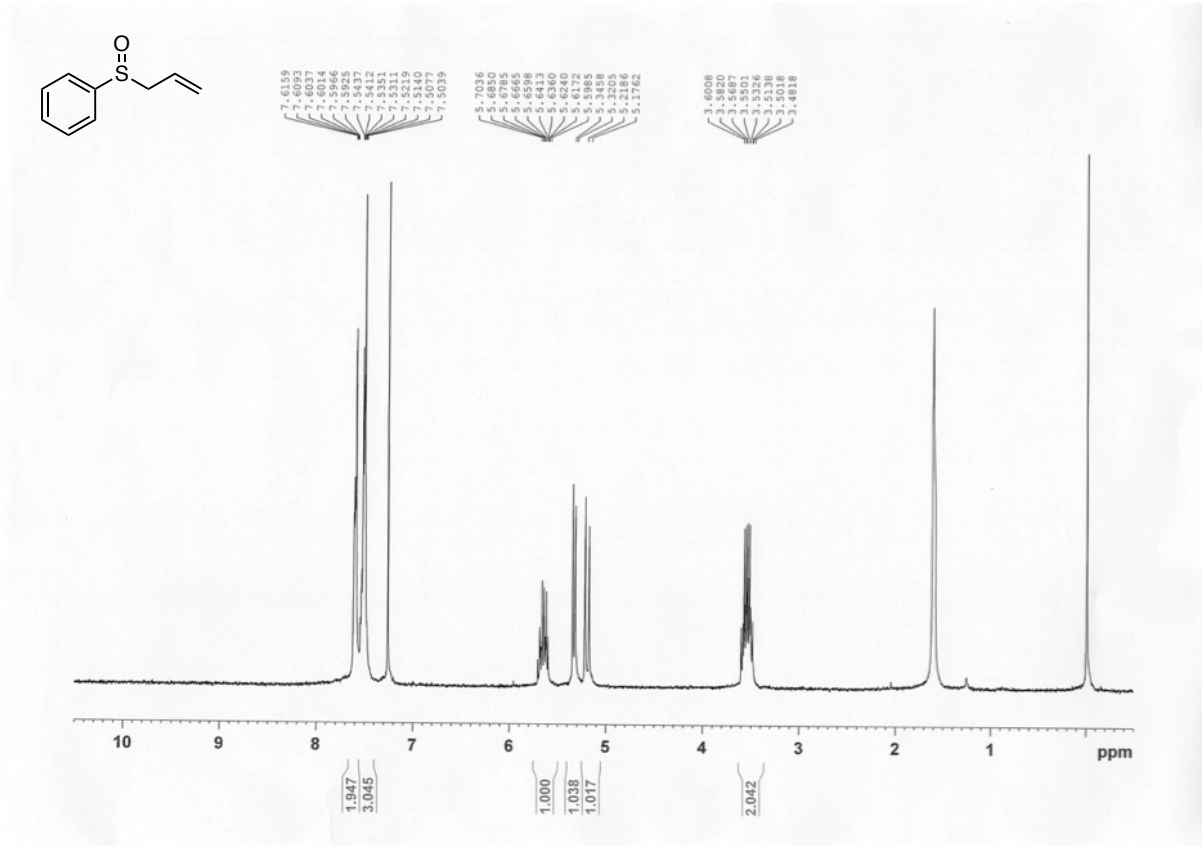


^{1}H NMR (500 MHz) and ^{13}C NMR (126 MHz) spectra of methyl 2,6-dimethylbenzenesulfinate (**10g**) ($CDCl_3$)

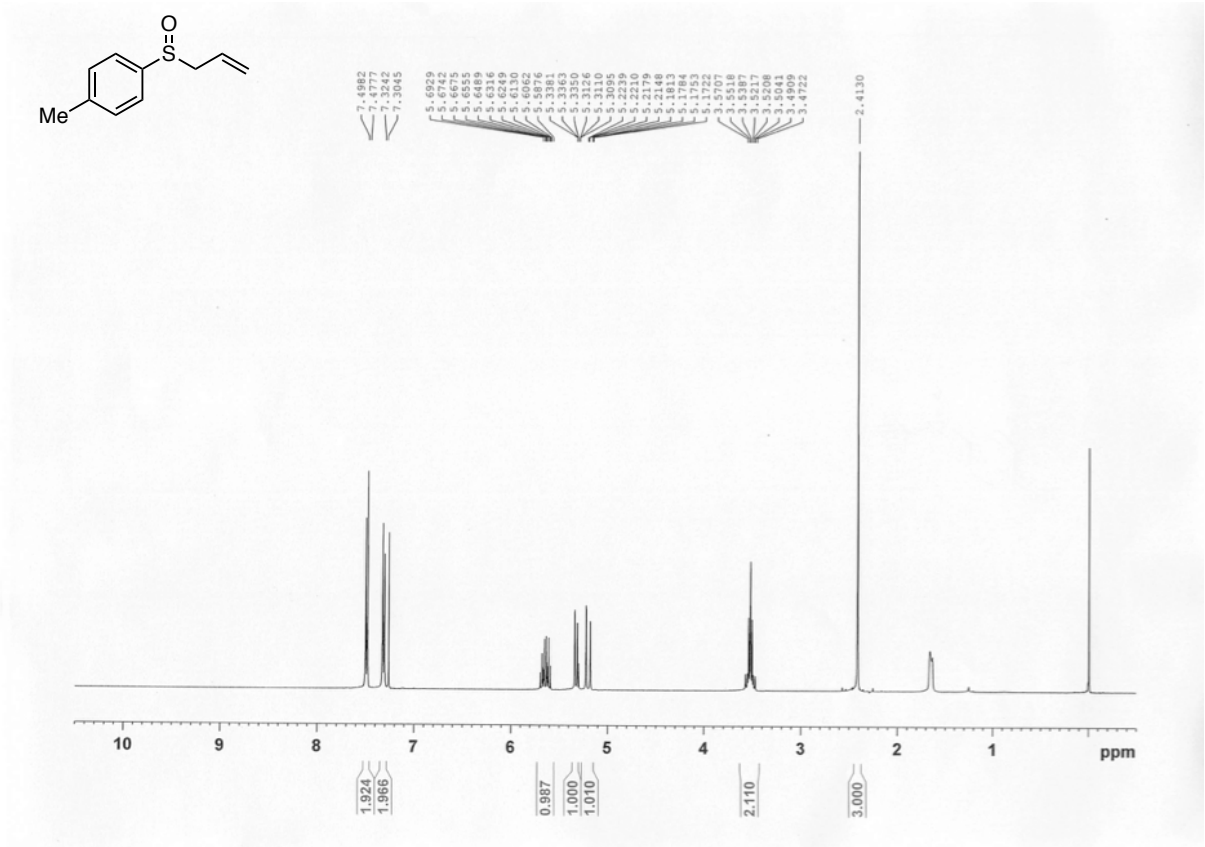




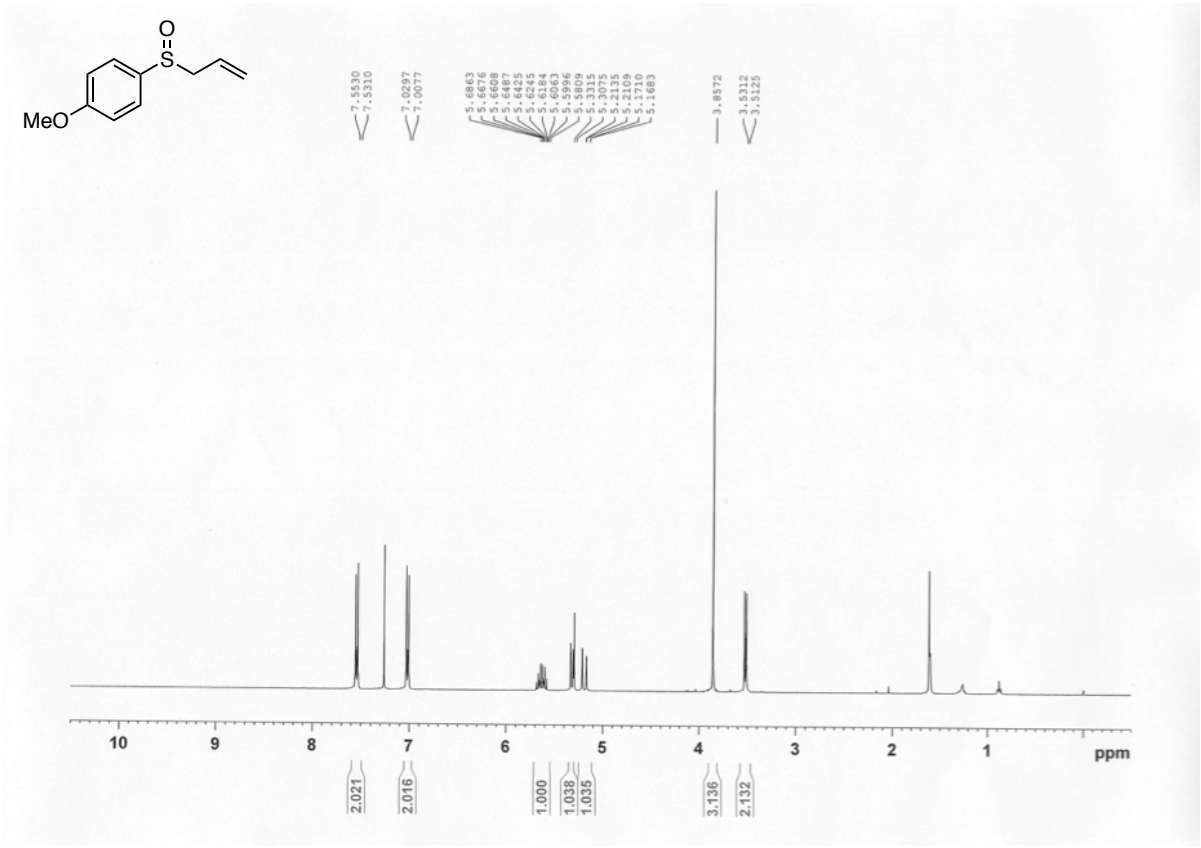
^{1}H NMR (400 MHz) spectra of allyl phenyl sulfoxide (**12a**) ($CDCl_3$)



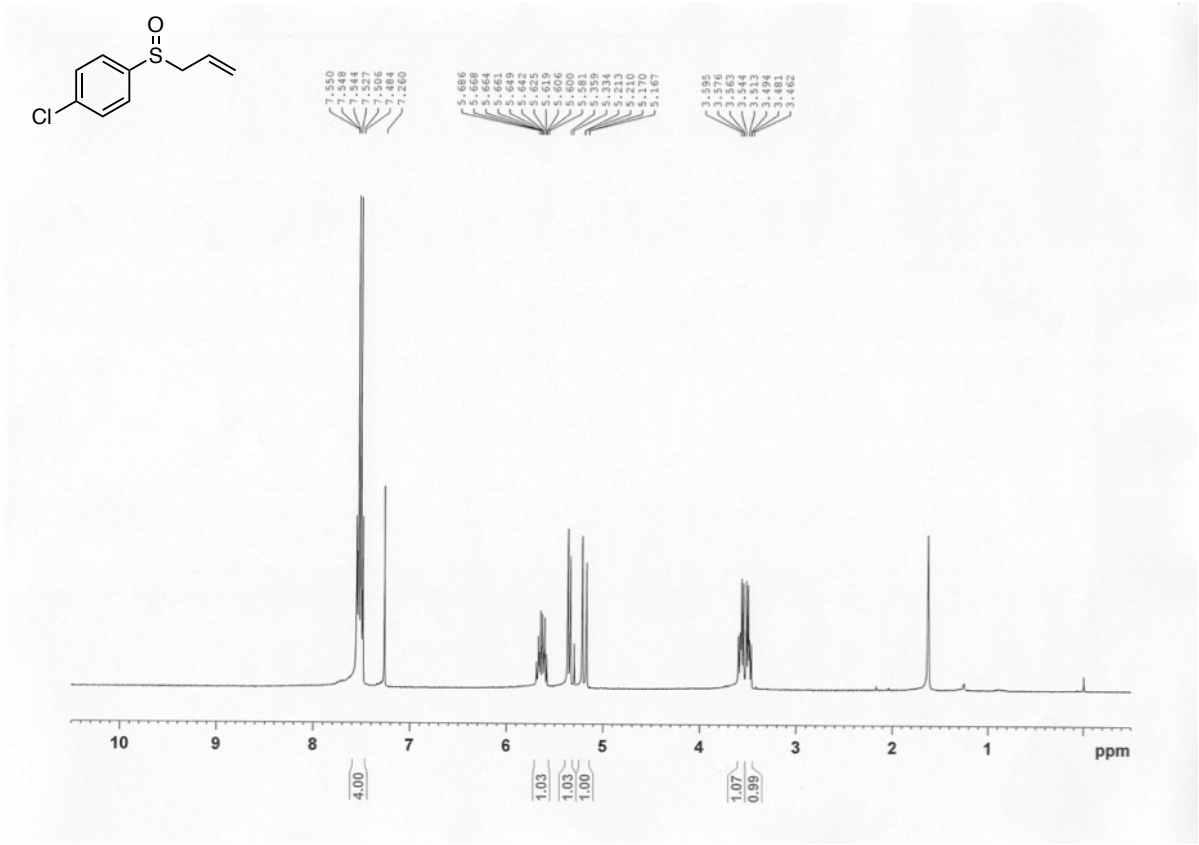
^{1}H NMR (400 MHz) spectra of allyl 4-tolyl sulfoxide (**12b**) ($CDCl_3$)



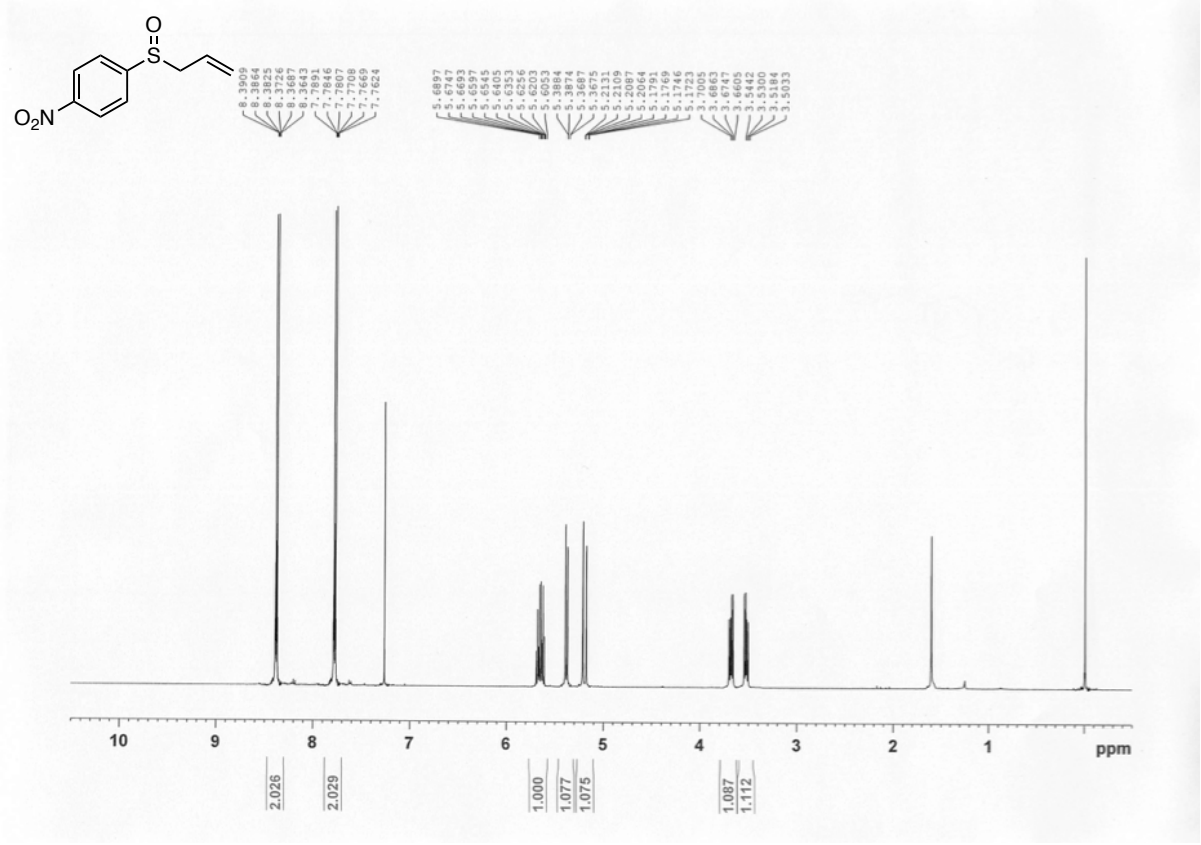
^{1}H NMR (400 MHz) spectra of allyl 4-methoxyphenyl sulfoxide (**12c**) ($CDCl_3$)



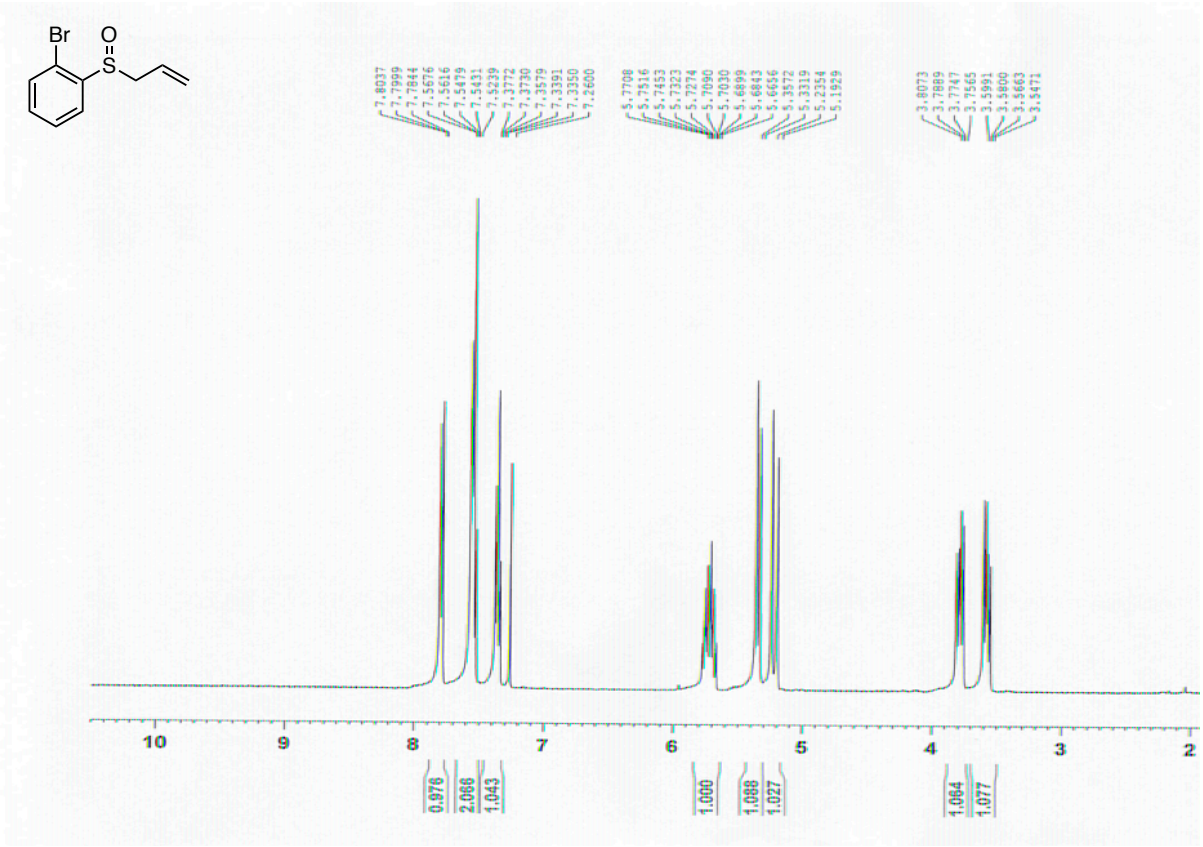
^{1}H NMR (400 MHz) spectra of allyl 4-chlorophenyl sulfoxide (**12d**) ($CDCl_3$)



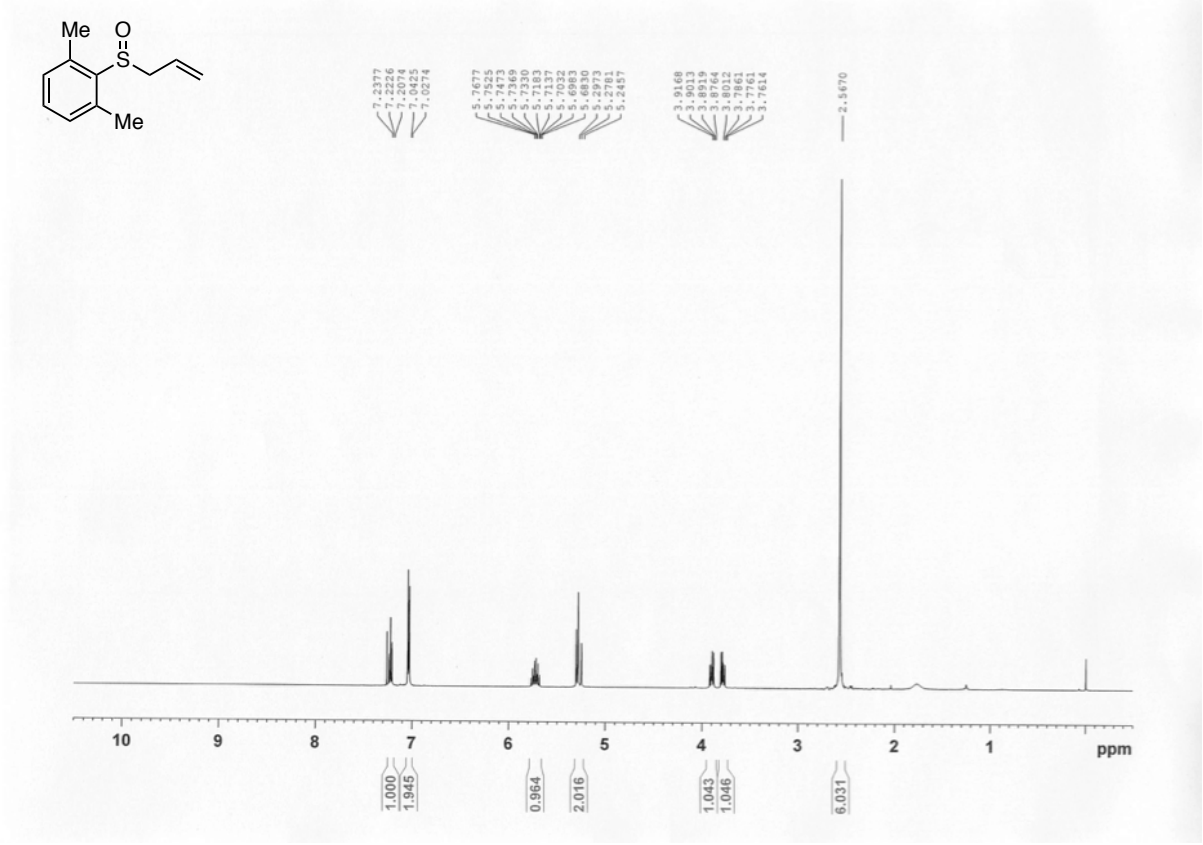
^{1}H NMR (400 MHz) of allyl 4-nitrophenyl sulfoxide (**12e**) ($CDCl_3$)



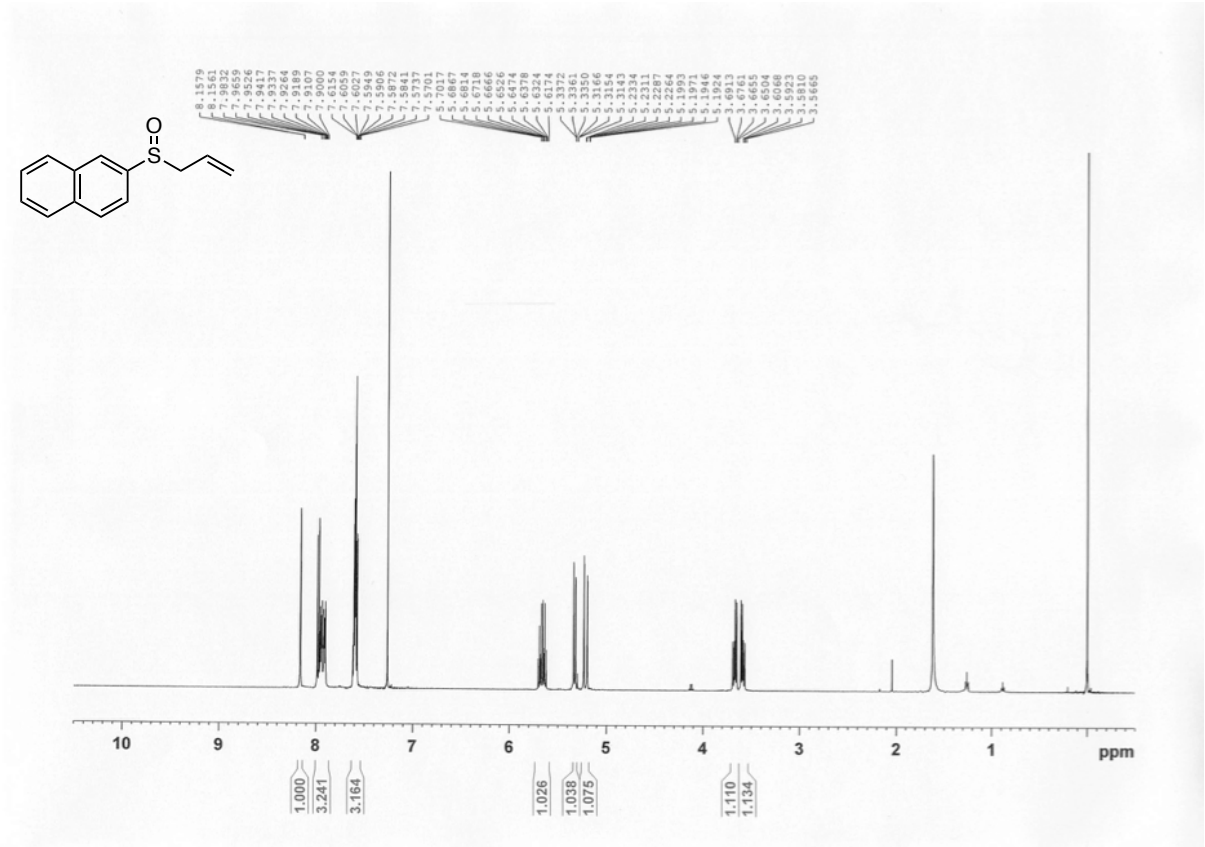
^{1}H NMR (400 MHz) spectra of allyl 2-bromophenyl sulfoxide (**12f**) ($CDCl_3$)



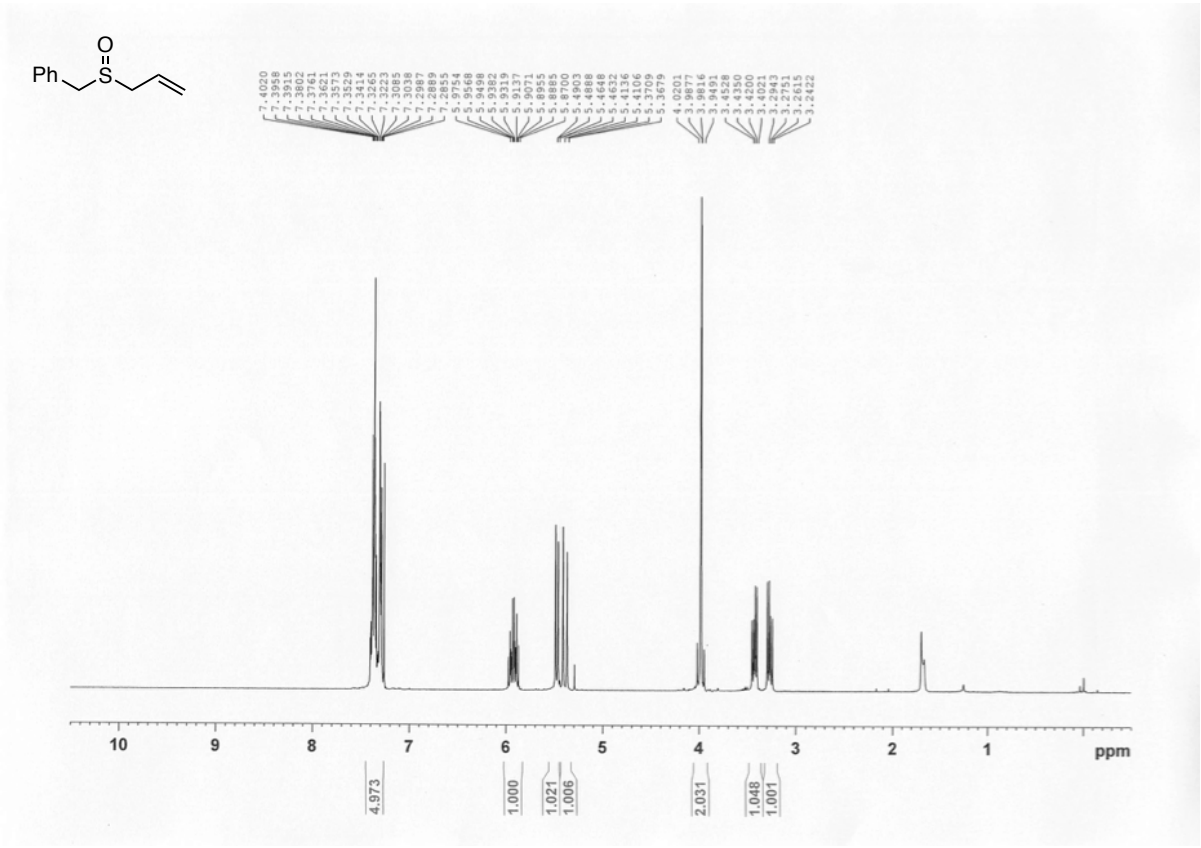
^{1}H NMR (400 MHz) spectra of allyl 2,6-dimethylphenyl sulfoxide (**12g**) ($CDCl_3$)



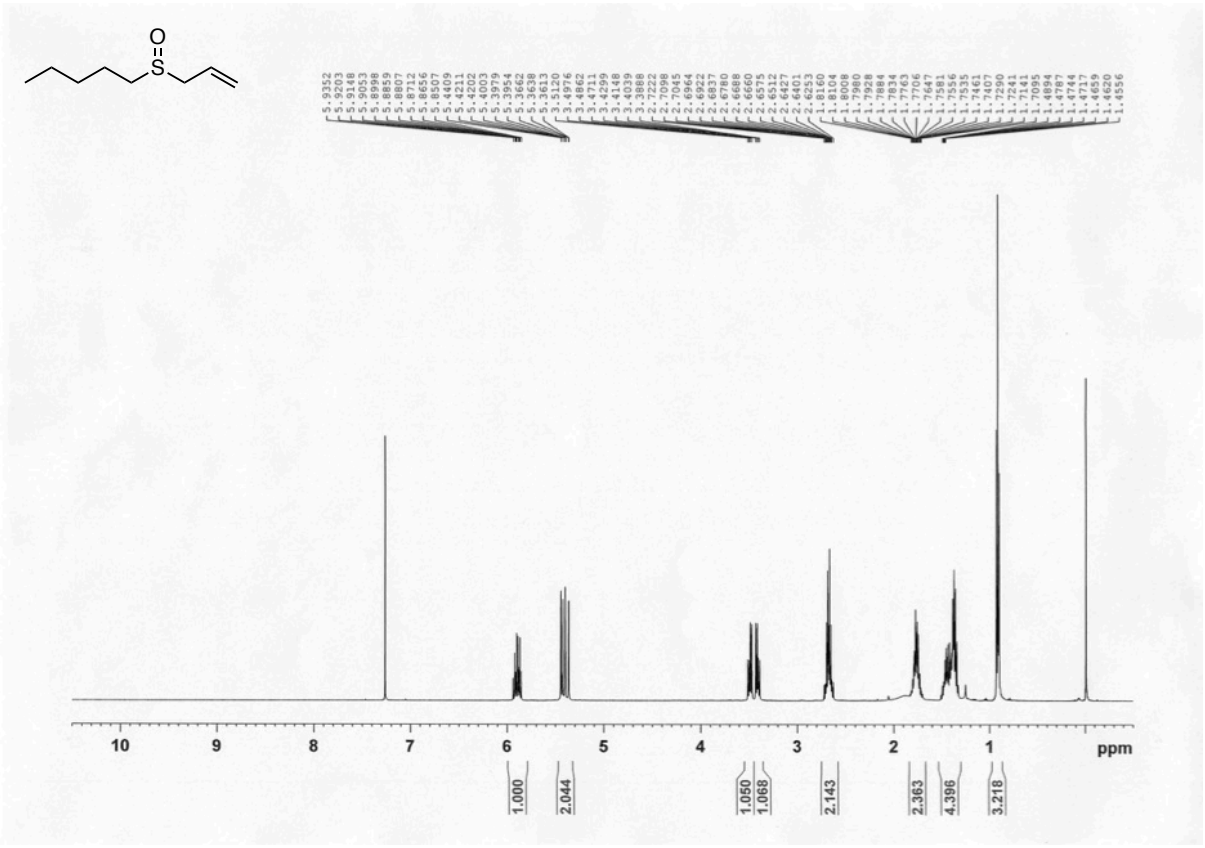
^{1}H NMR (400 MHz) spectra of allyl 2-naphthyl sulfoxide (**12h**) ($CDCl_3$)

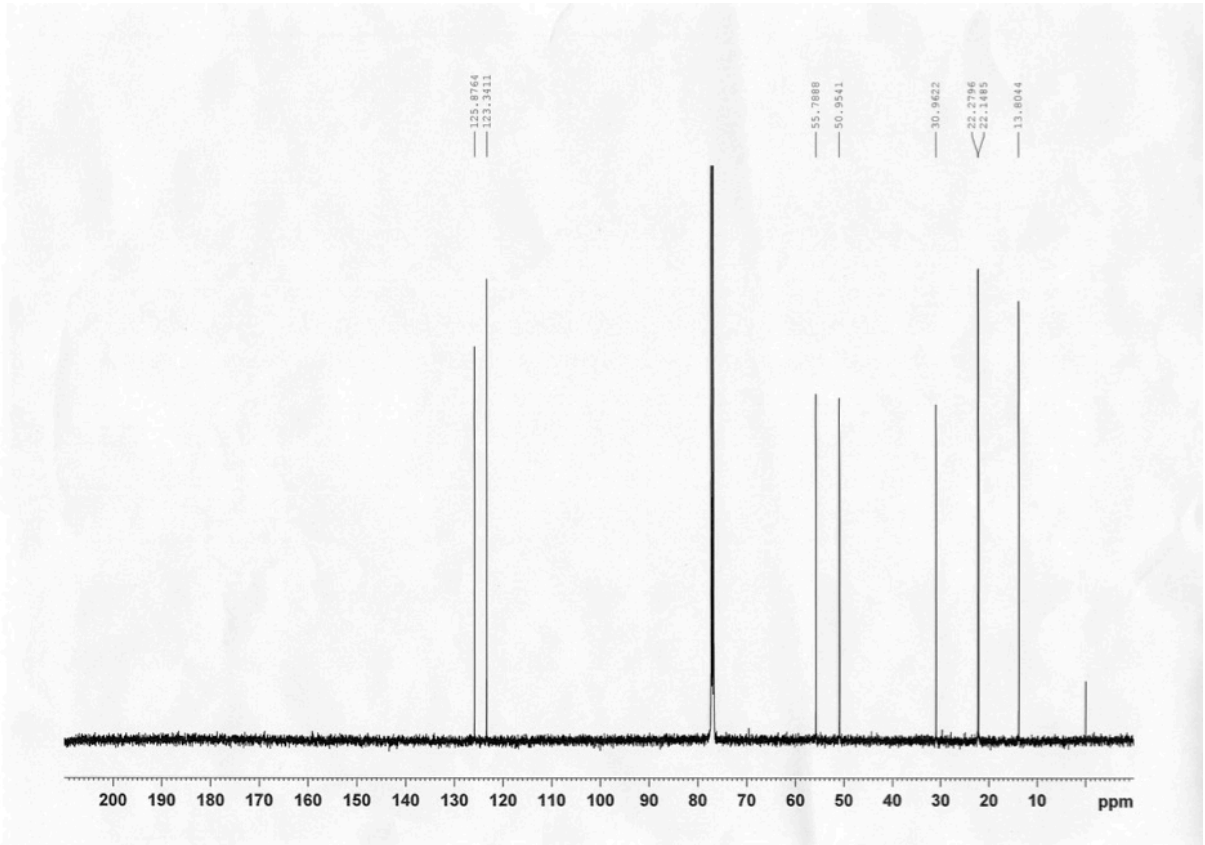


^{1}H NMR (400 MHz) spectra of allyl benzyl sulfoxide (**12i**) ($CDCl_3$)

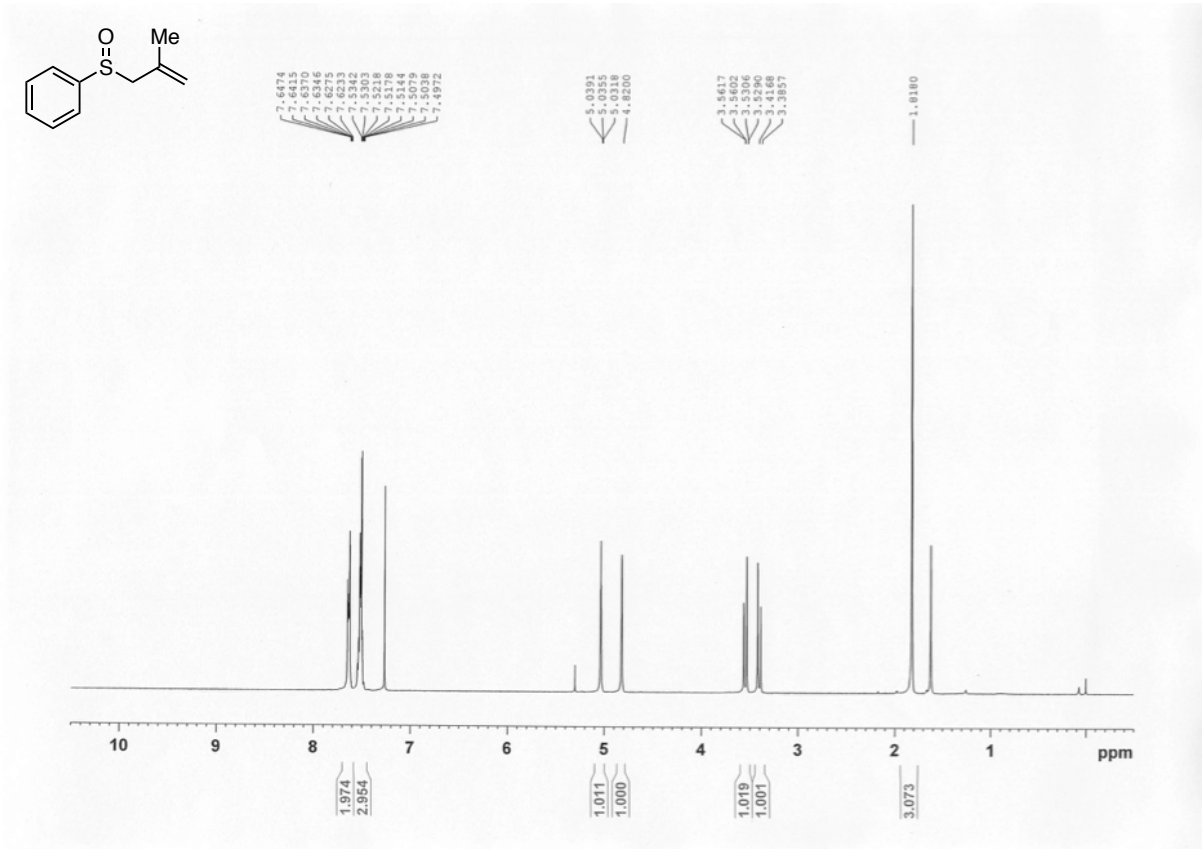


^{1}H NMR (500 MHz) and ^{13}C NMR (126 MHz) spectra of allyl 1-pentyl sulfoxide (**12j**) ($CDCl_3$)

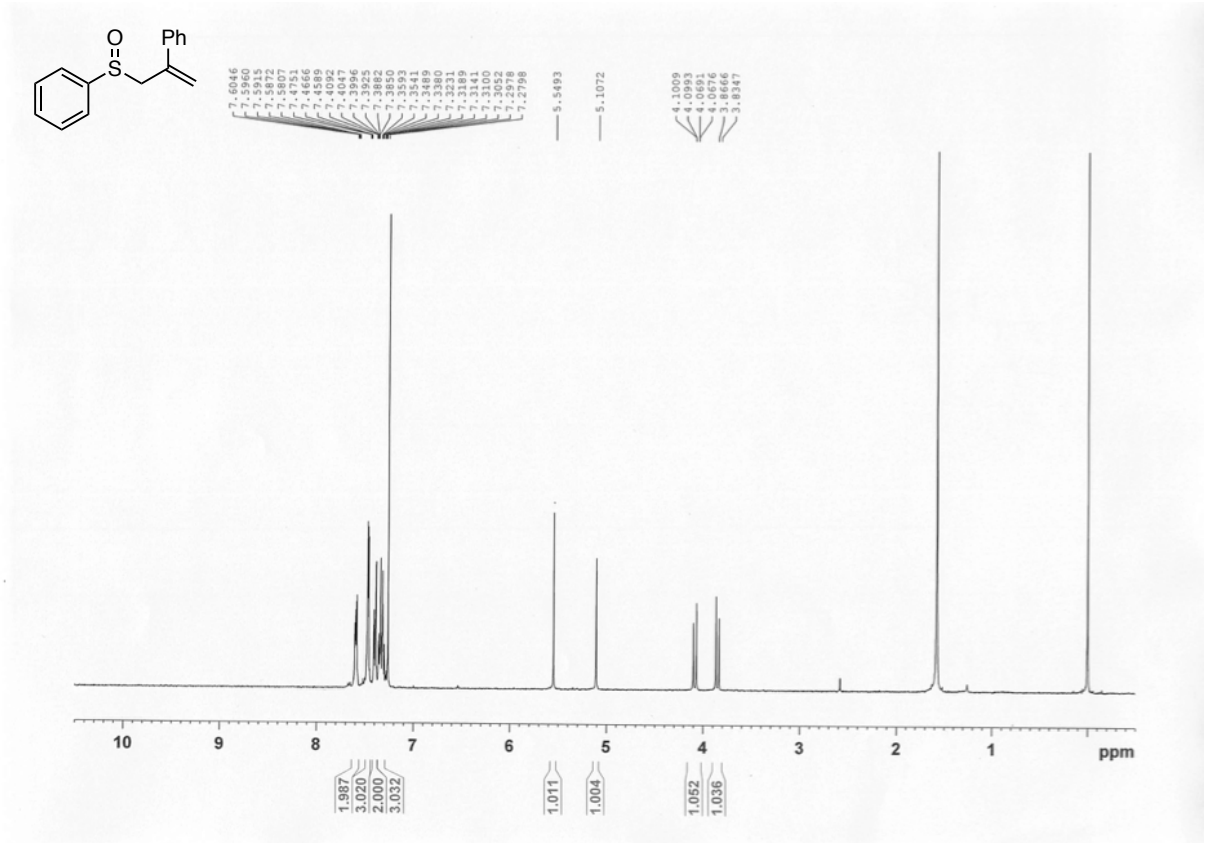




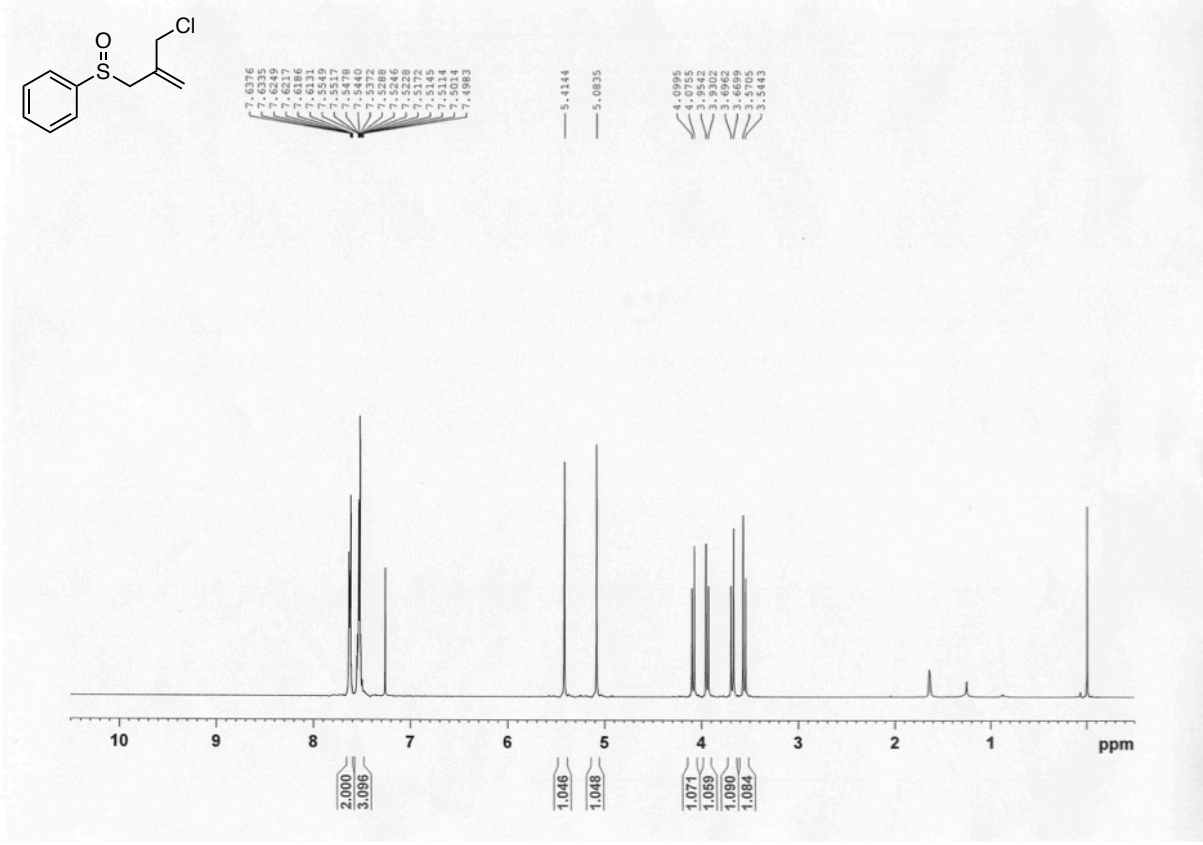
^{1}H NMR (400 MHz) spectra of 2-methylallyl phenyl sulfoxide (**12k**) ($CDCl_3$)

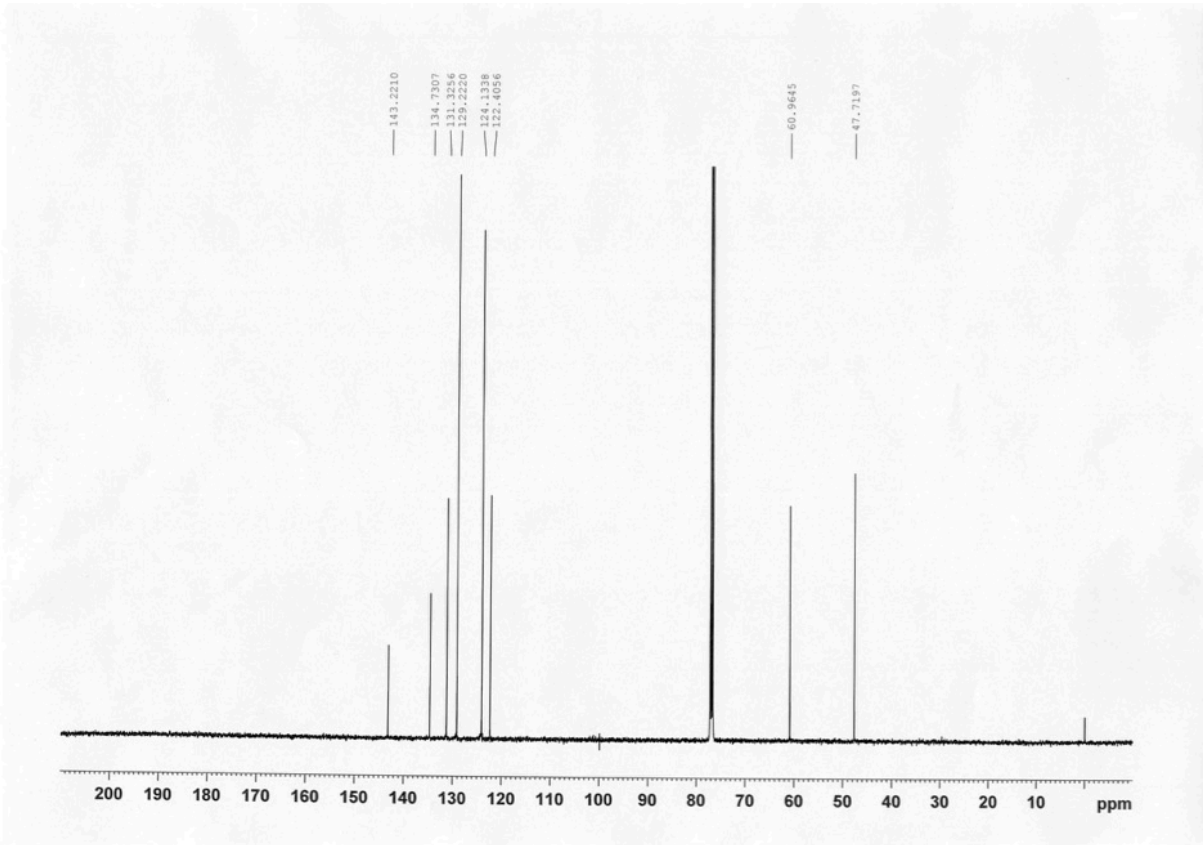


^{1}H NMR (400 MHz) spectra of phenyl 2-phenylallyl sulfoxide (**12l**) ($CDCl_3$)

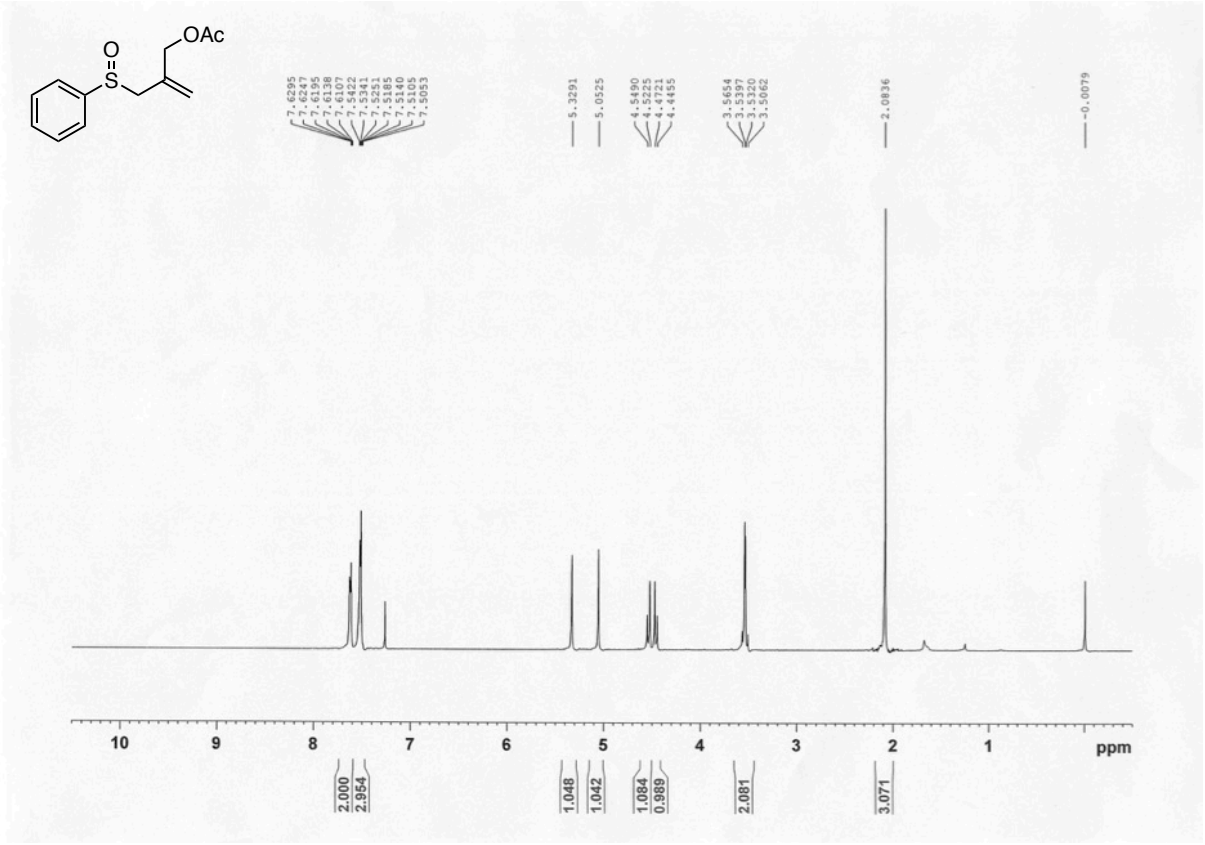


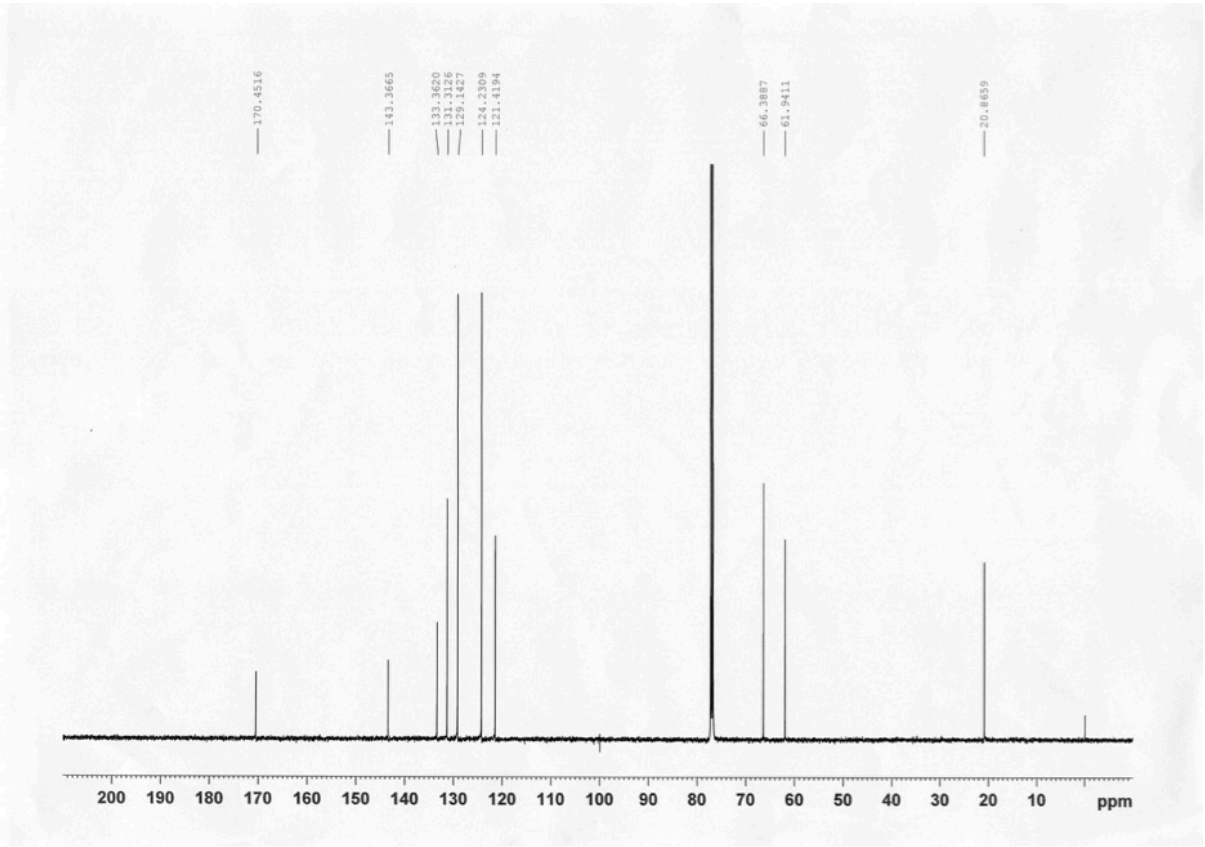
^{1}H NMR (500 MHz) and ^{13}C NMR (126 MHz) spectra of 2-(chloromethyl)allyl phenyl sulfoxide (**12m**) ($CDCl_3$)



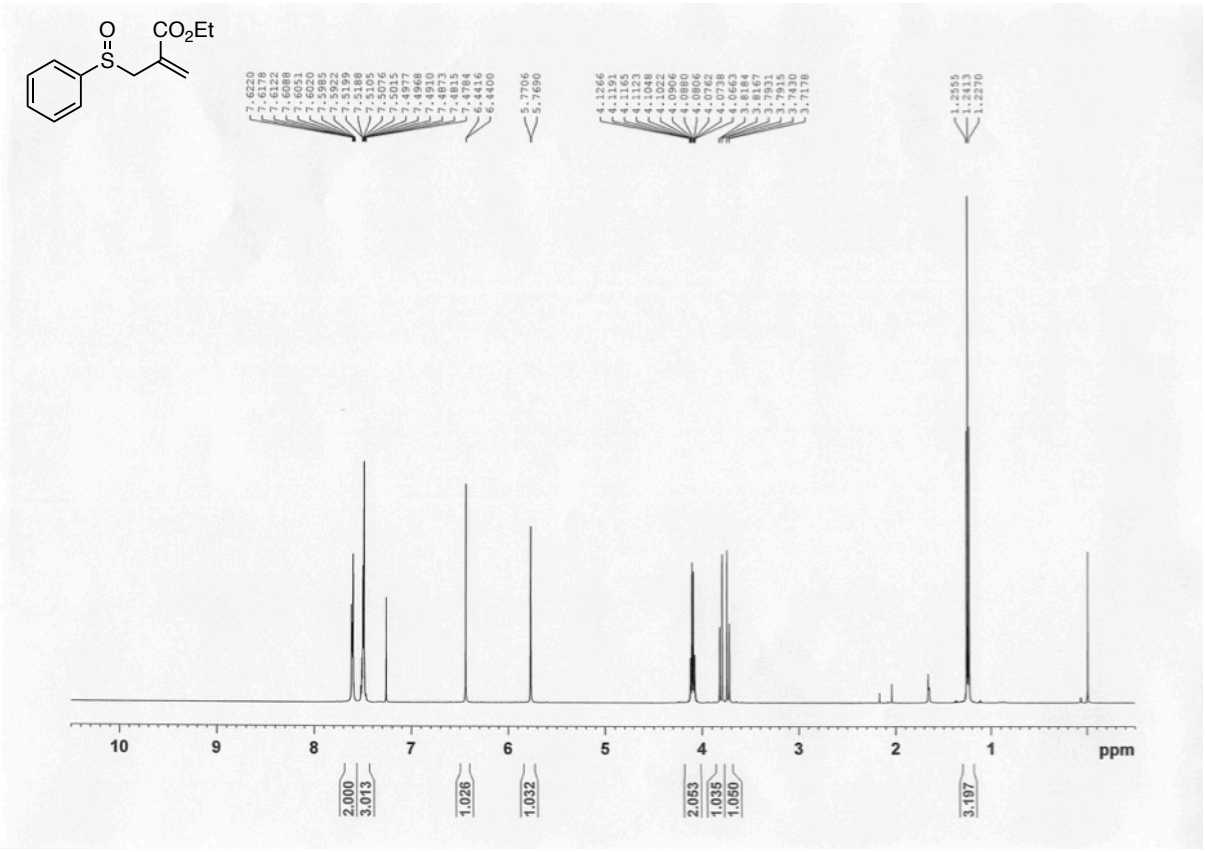


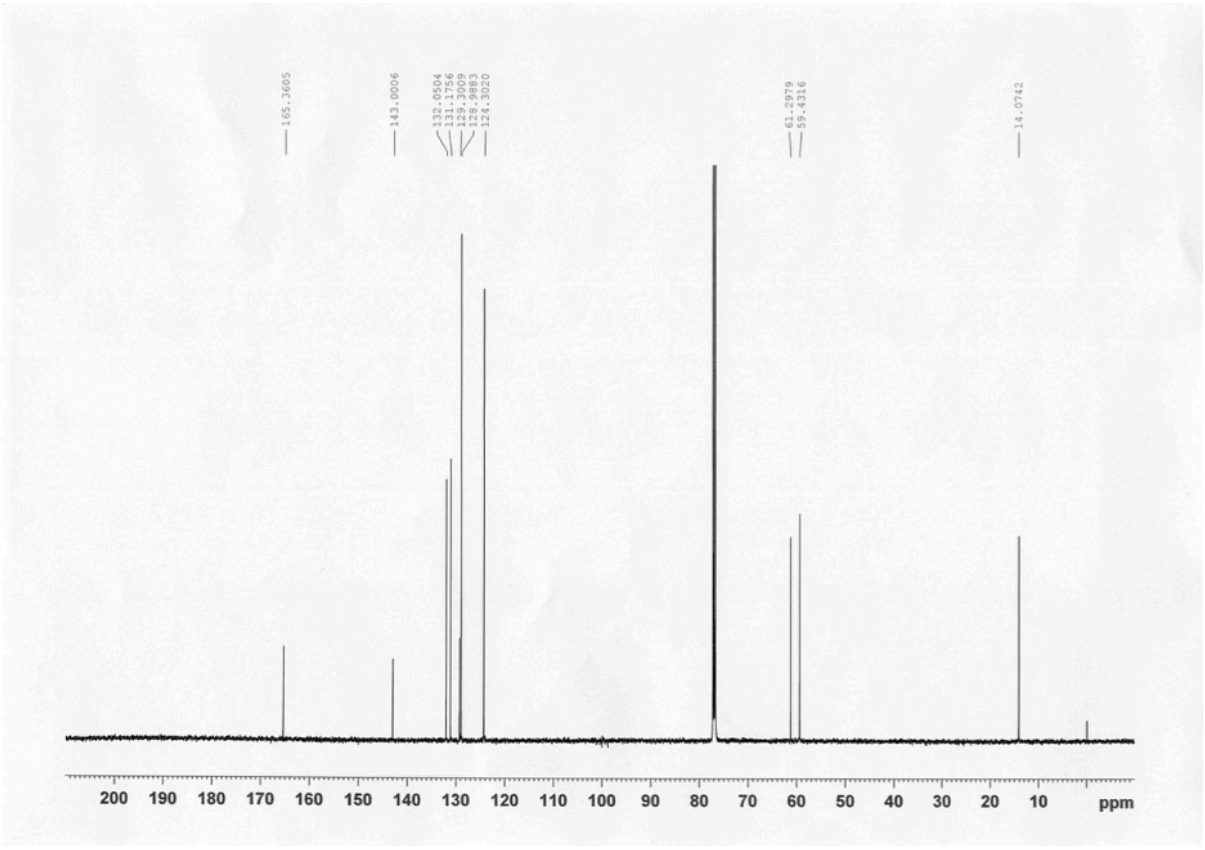
^{1}H NMR (500 MHz) and ^{13}C NMR (126 MHz) spectra of 2-(acetoxymethyl)allyl phenyl sulfoxide (**12n**) ($CDCl_3$)



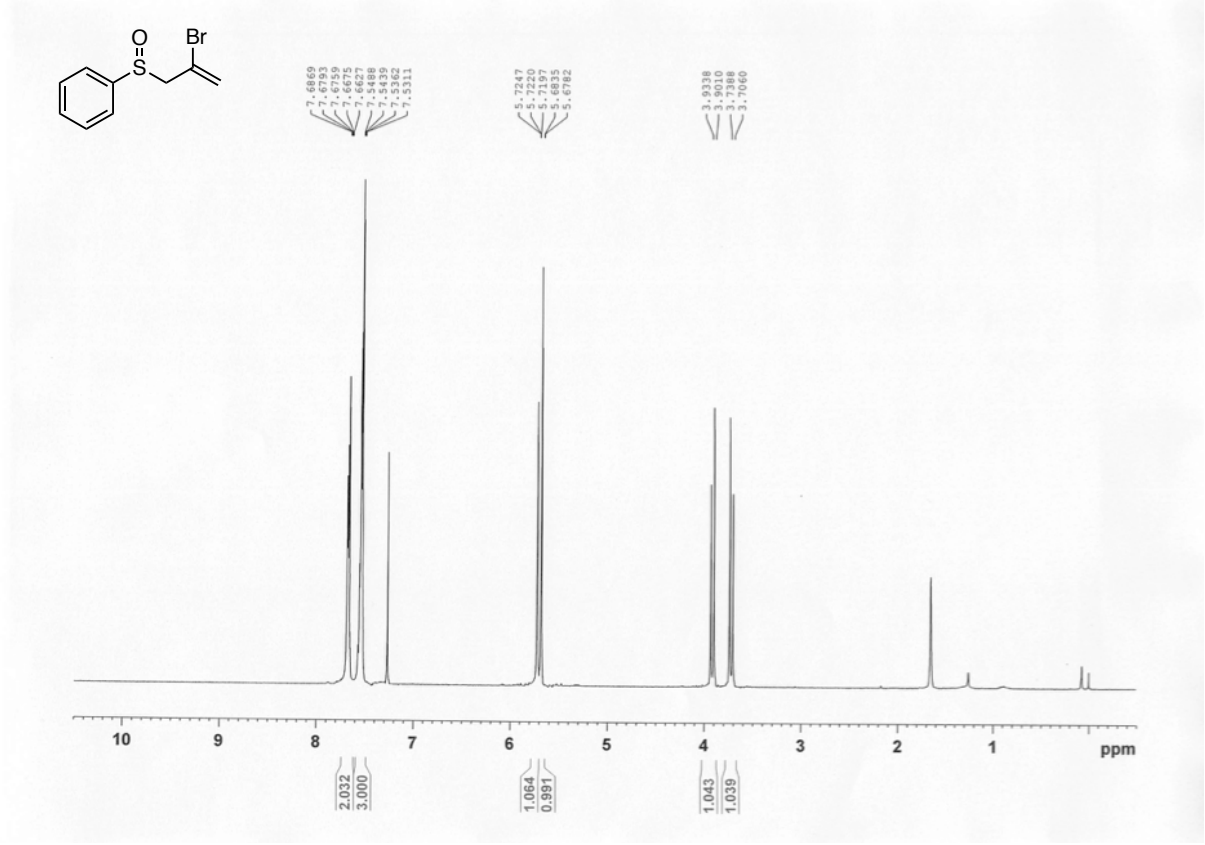


^{1}H NMR (500 MHz) and ^{13}C NMR (126 MHz) spectra of 2-(ethoxycarbonyl)allyl phenyl sulfoxide (**12o**) ($CDCl_3$)

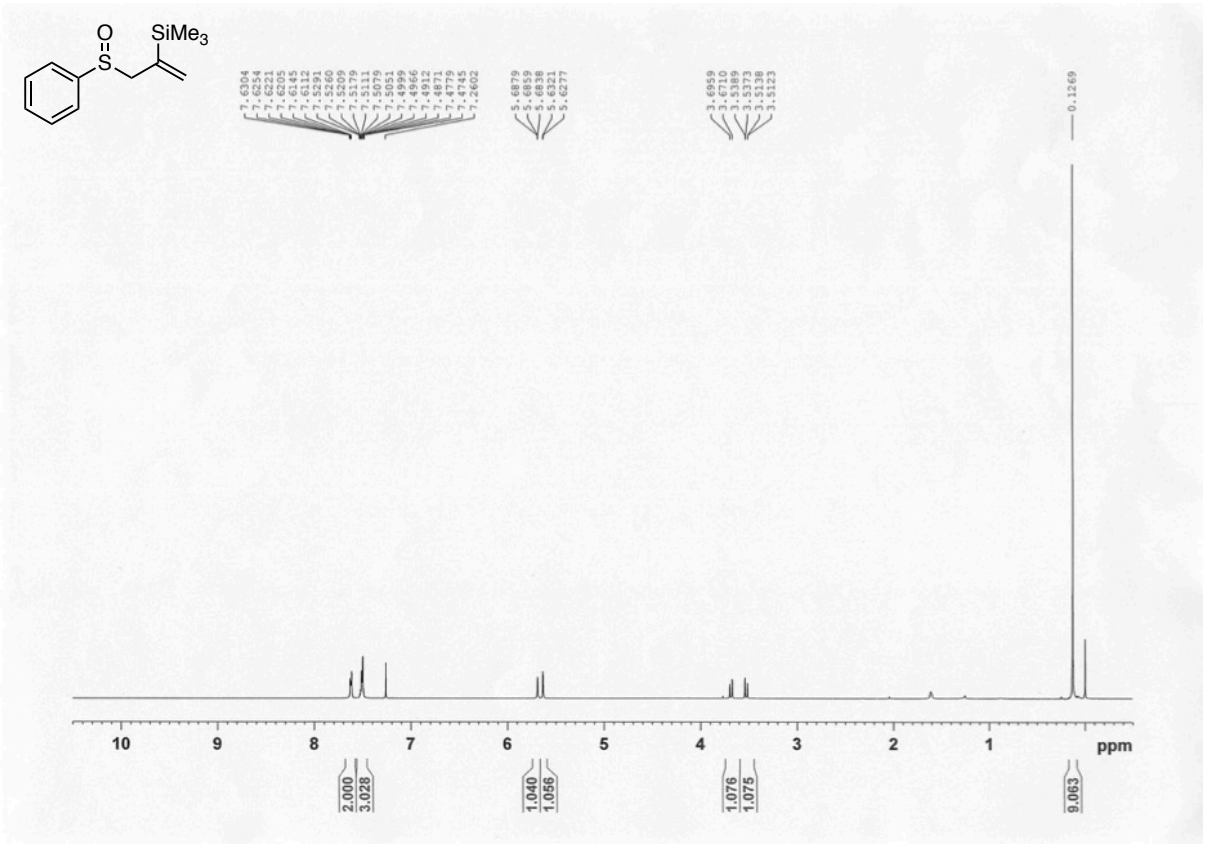


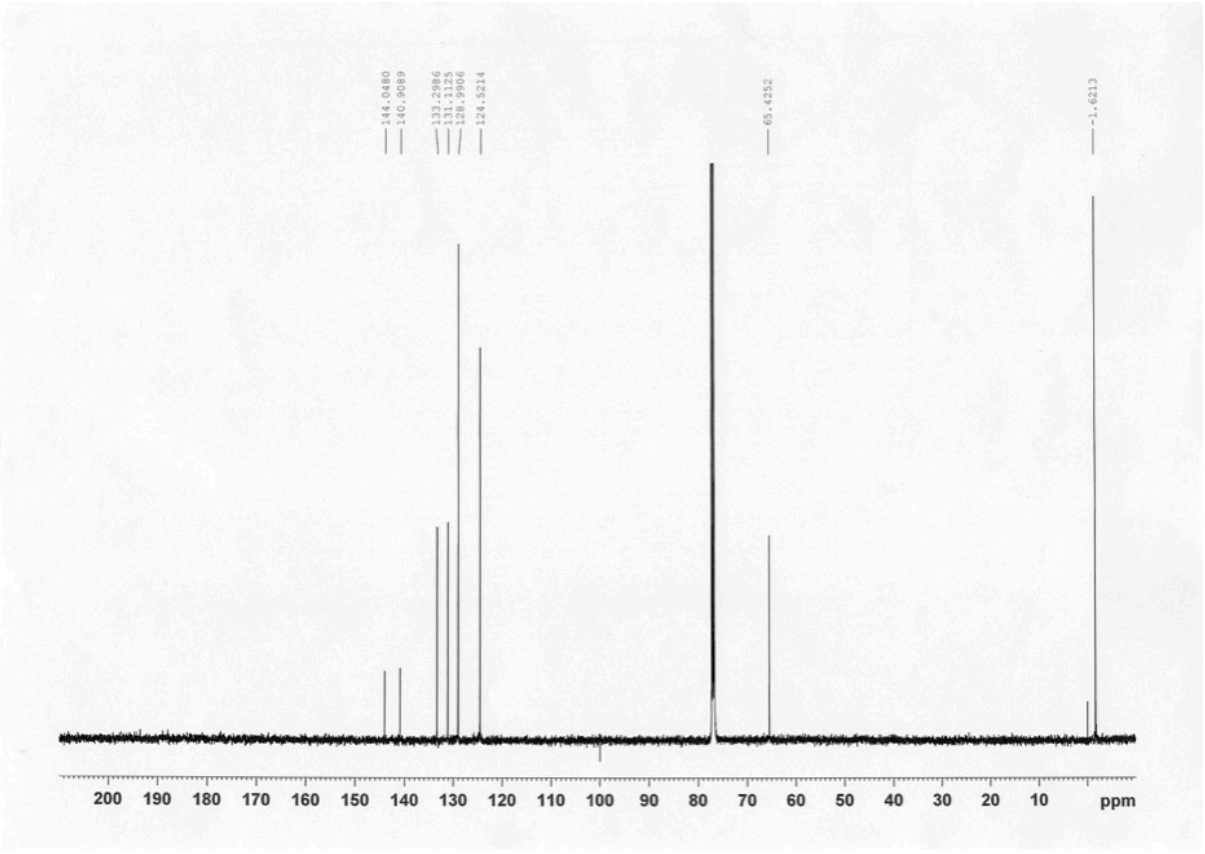


^{1}H NMR (400 MHz) spectra of 2-bromoallyl phenyl sulfoxide (**12p**) ($CDCl_3$)

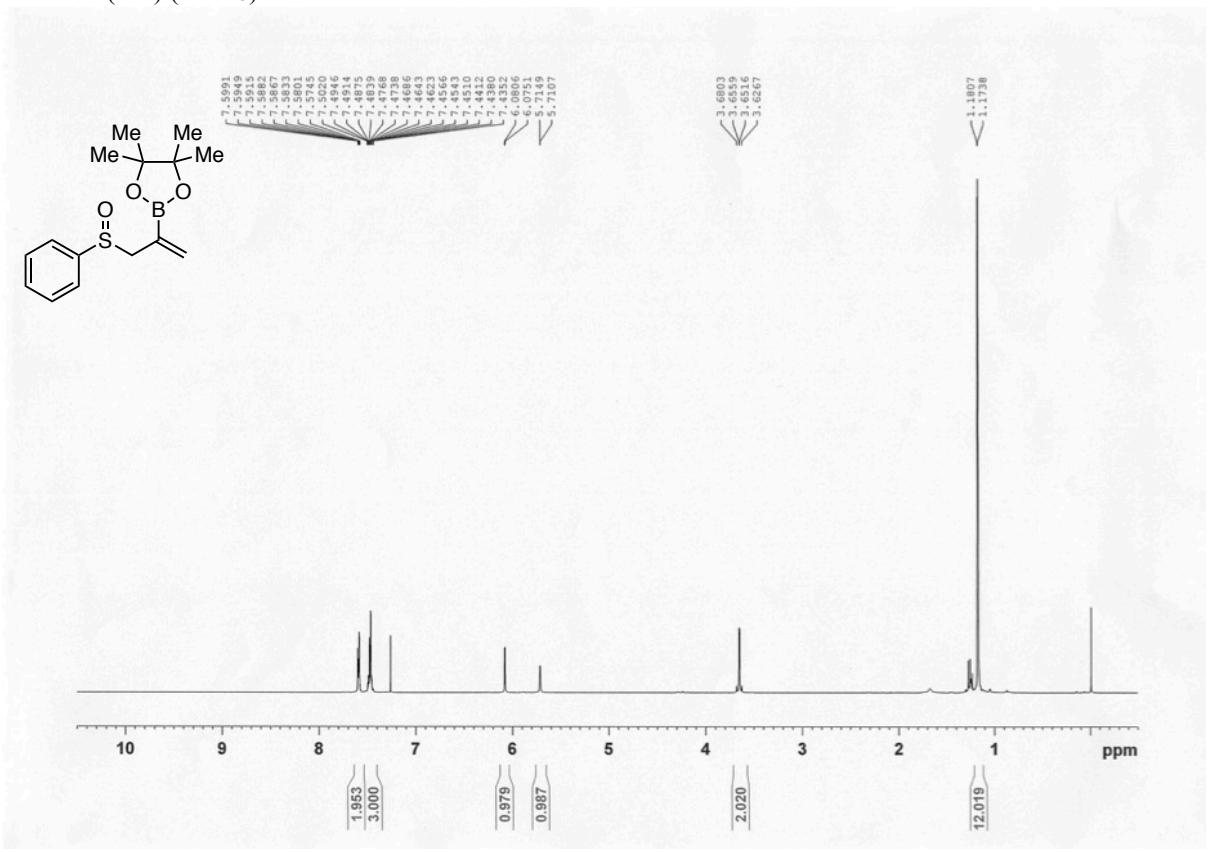


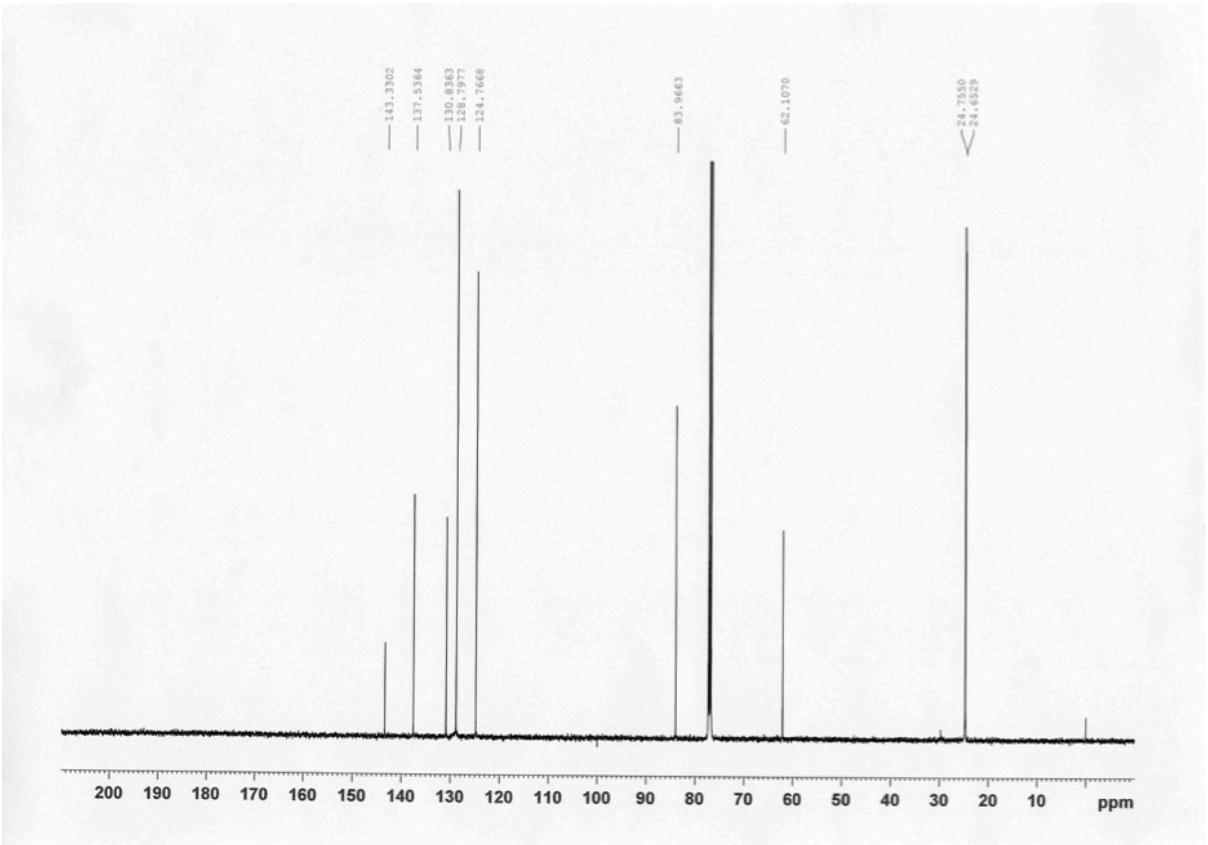
^{1}H NMR (500 MHz) and ^{13}C NMR (126 MHz) spectra of phenyl 2-(trimethylsilyl)allyl sulfoxide (**12q**) ($CDCl_3$)



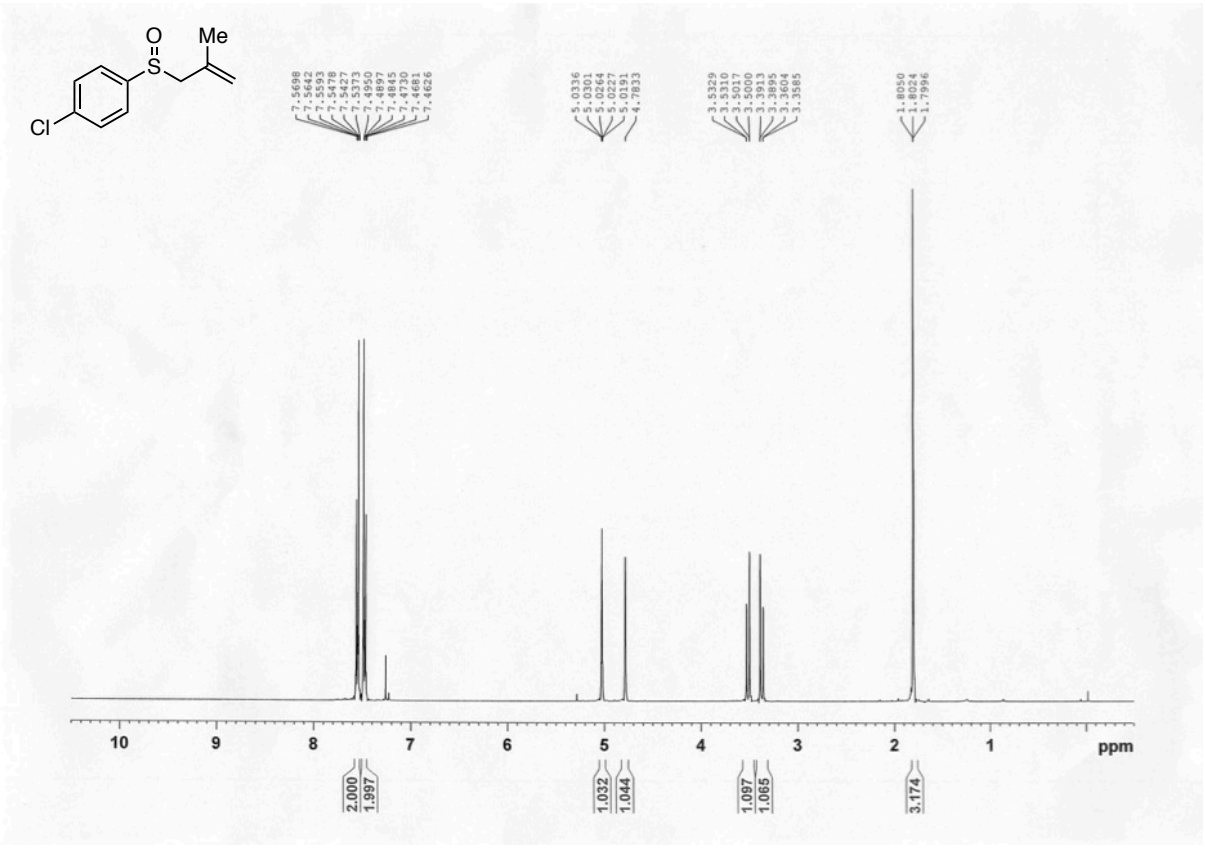


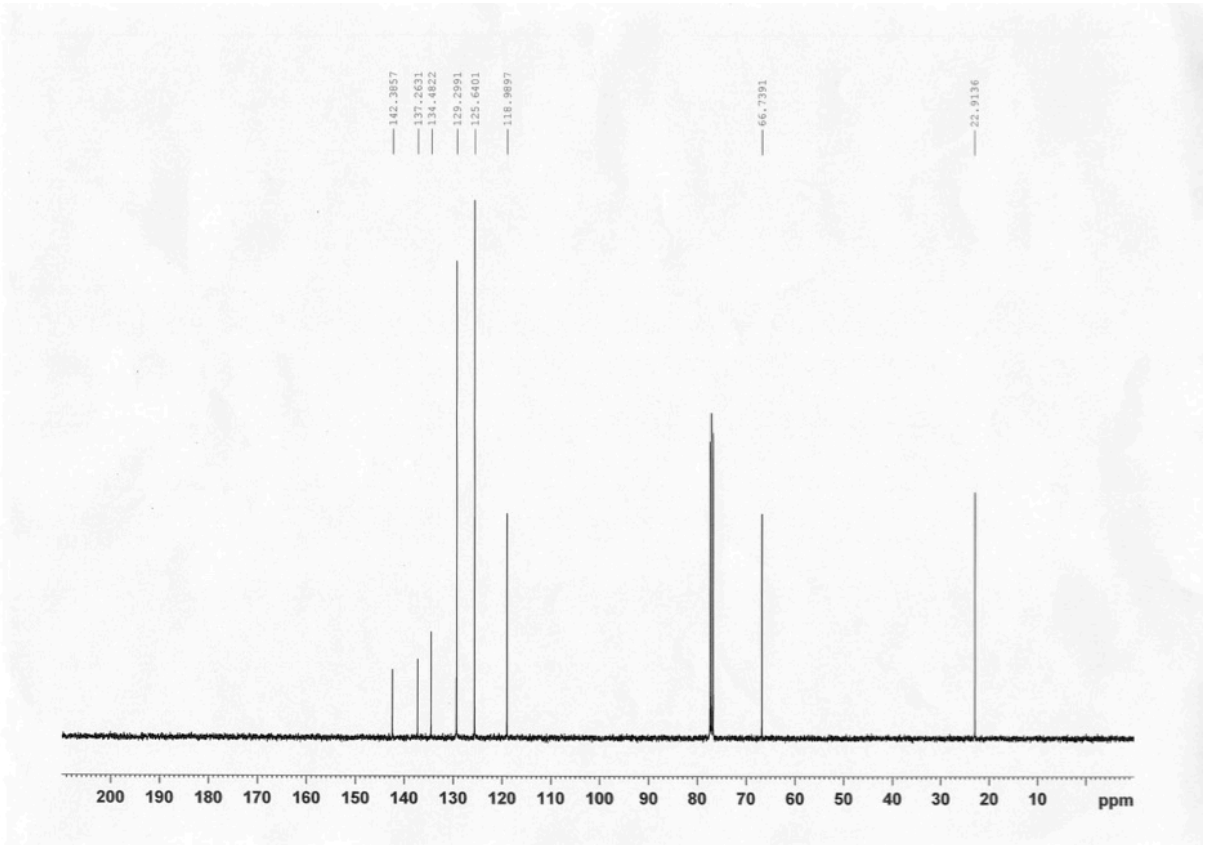
^{1}H NMR (500 MHz) and ^{13}C NMR (126 MHz) spectra of phenyl 2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolyl)allyl sulfoxide (**12r**) ($CDCl_3$)



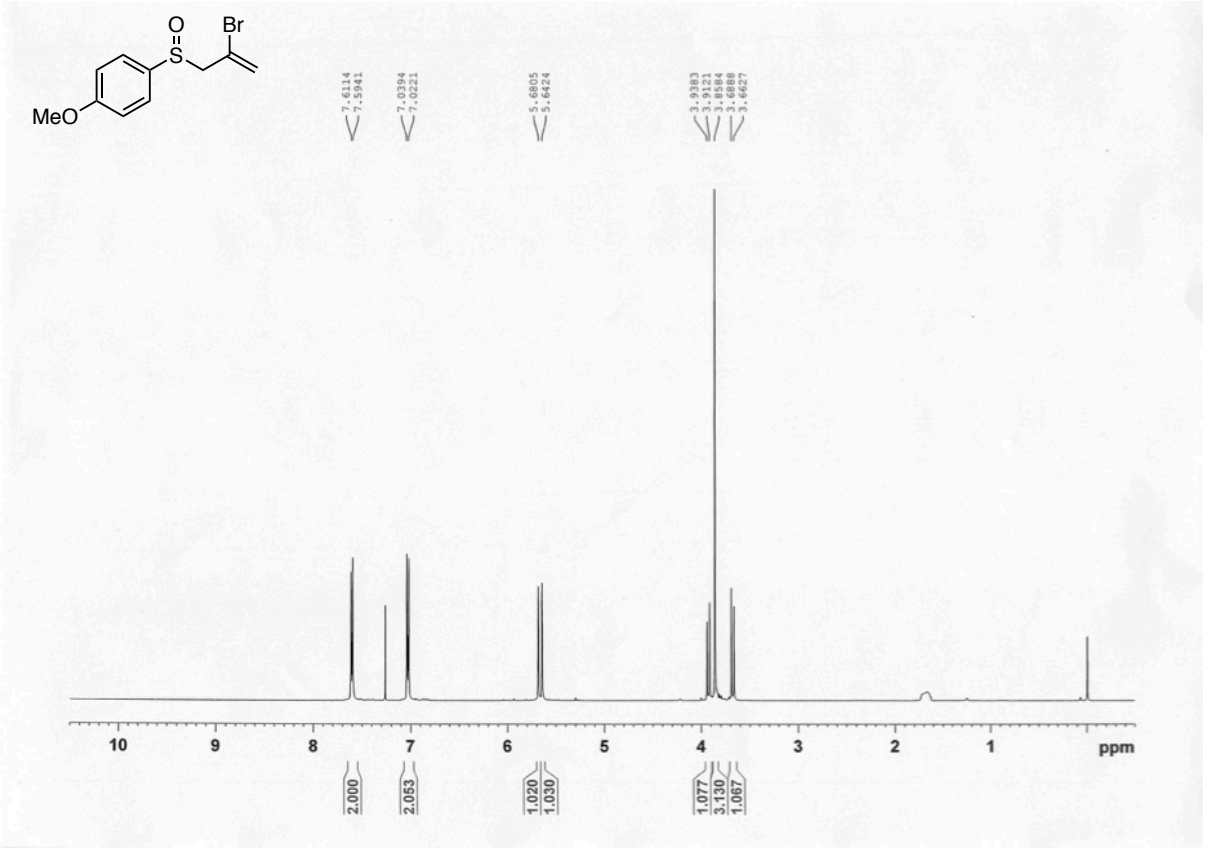


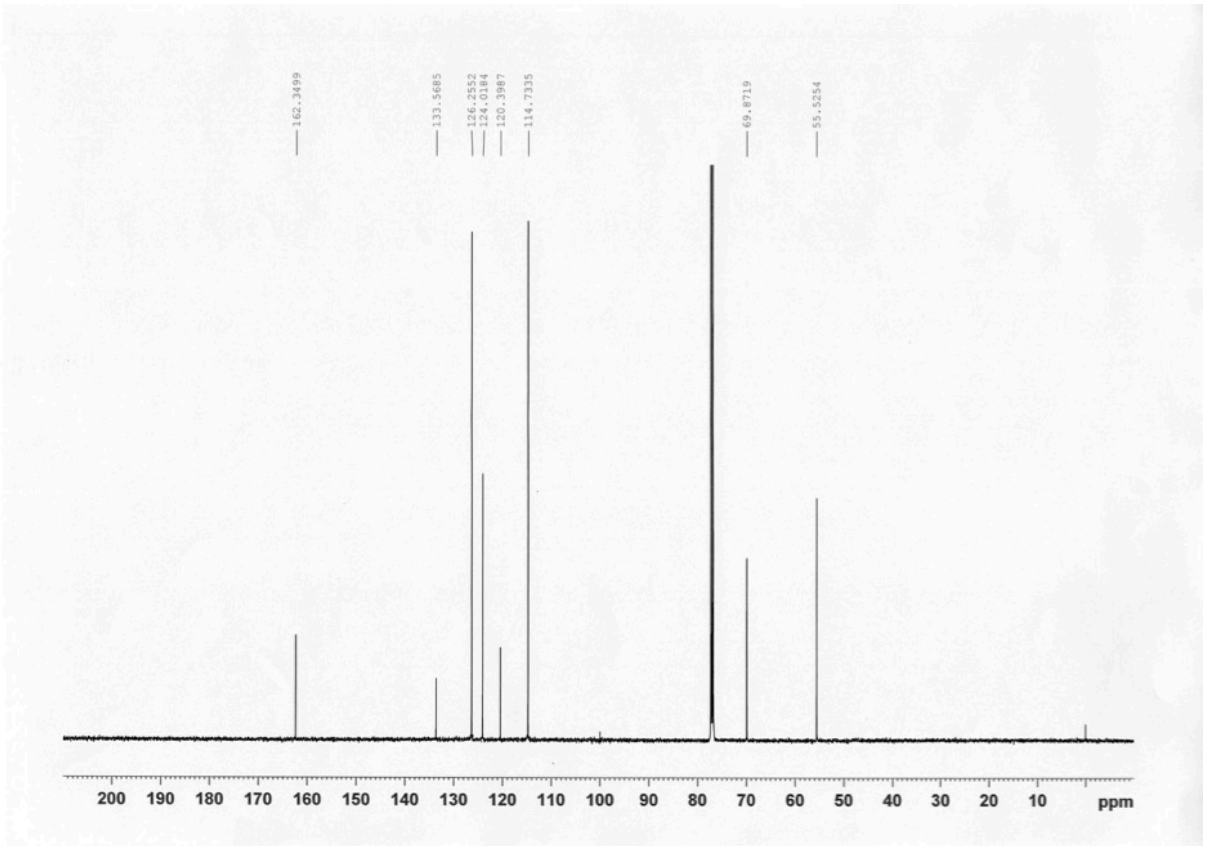
^{1}H NMR (400 MHz) and ^{13}C NMR (101 MHz) spectra of 4-chlorophenyl 2-methylallyl sulfoxide (**12s**) ($CDCl_3$)



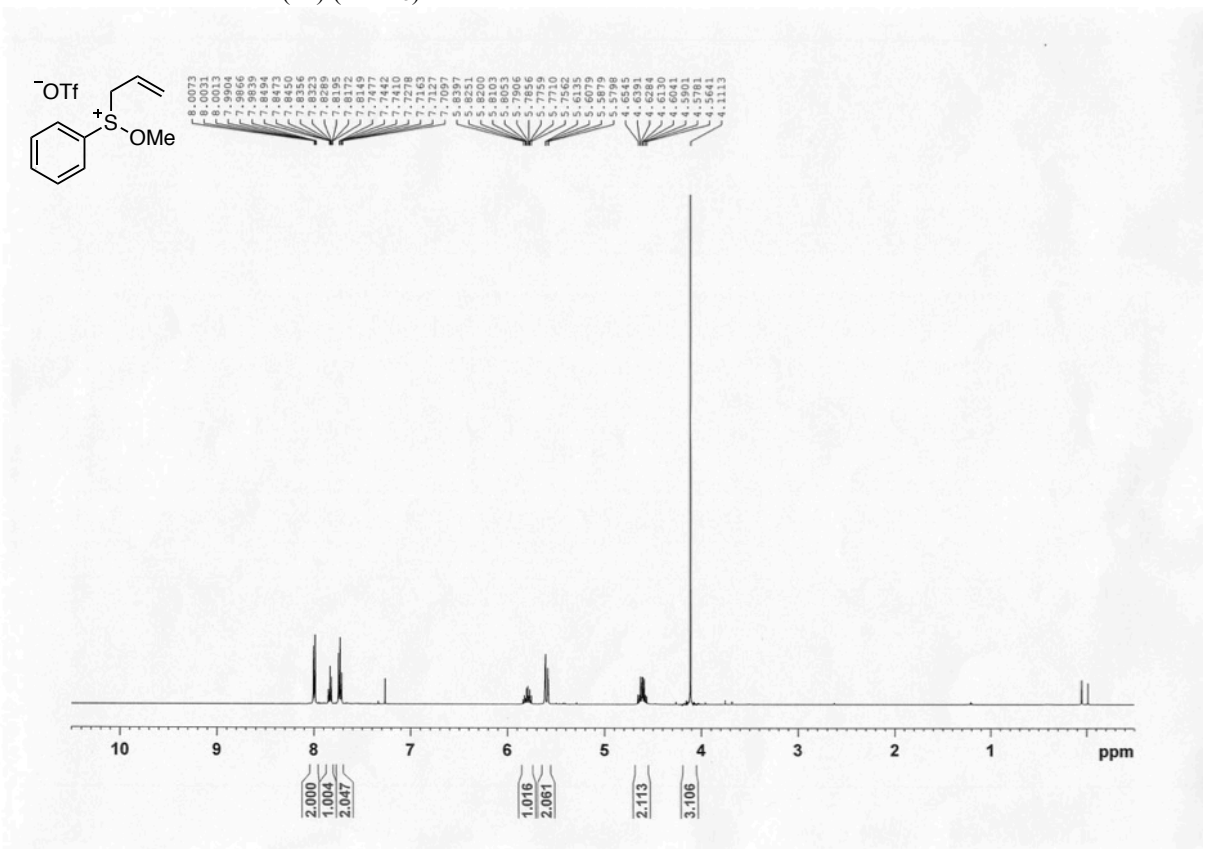


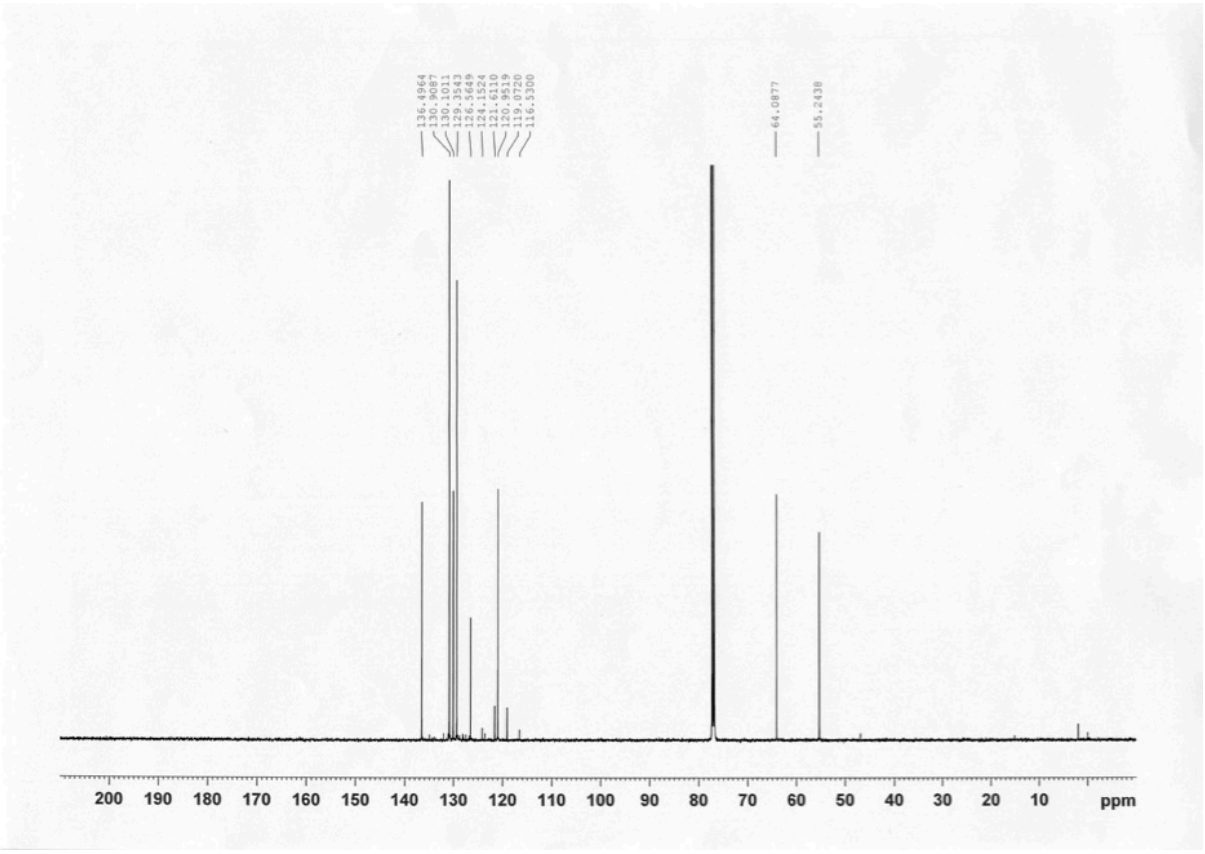
^{1}H NMR (500 MHz) and ^{13}C NMR (126 MHz) spectra of 2-bromoallyl 4-methoxyphenyl sulfoxide (**12t**) ($CDCl_3$)



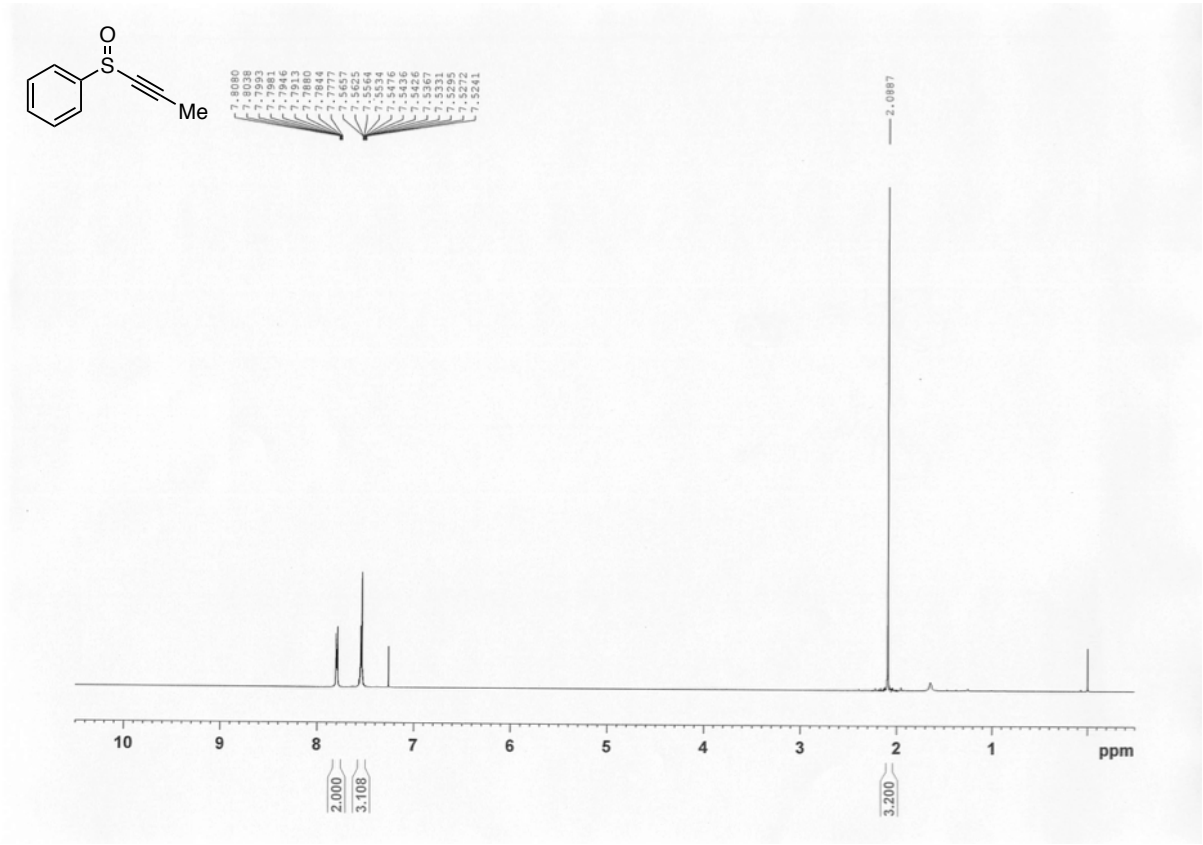


^{1}H NMR (500 MHz) and ^{13}C NMR (126 MHz) spectra of allyl(methoxy)(phenyl)sulfonium trifluoromethanesulfonate (**13**) ($CDCl_3$)

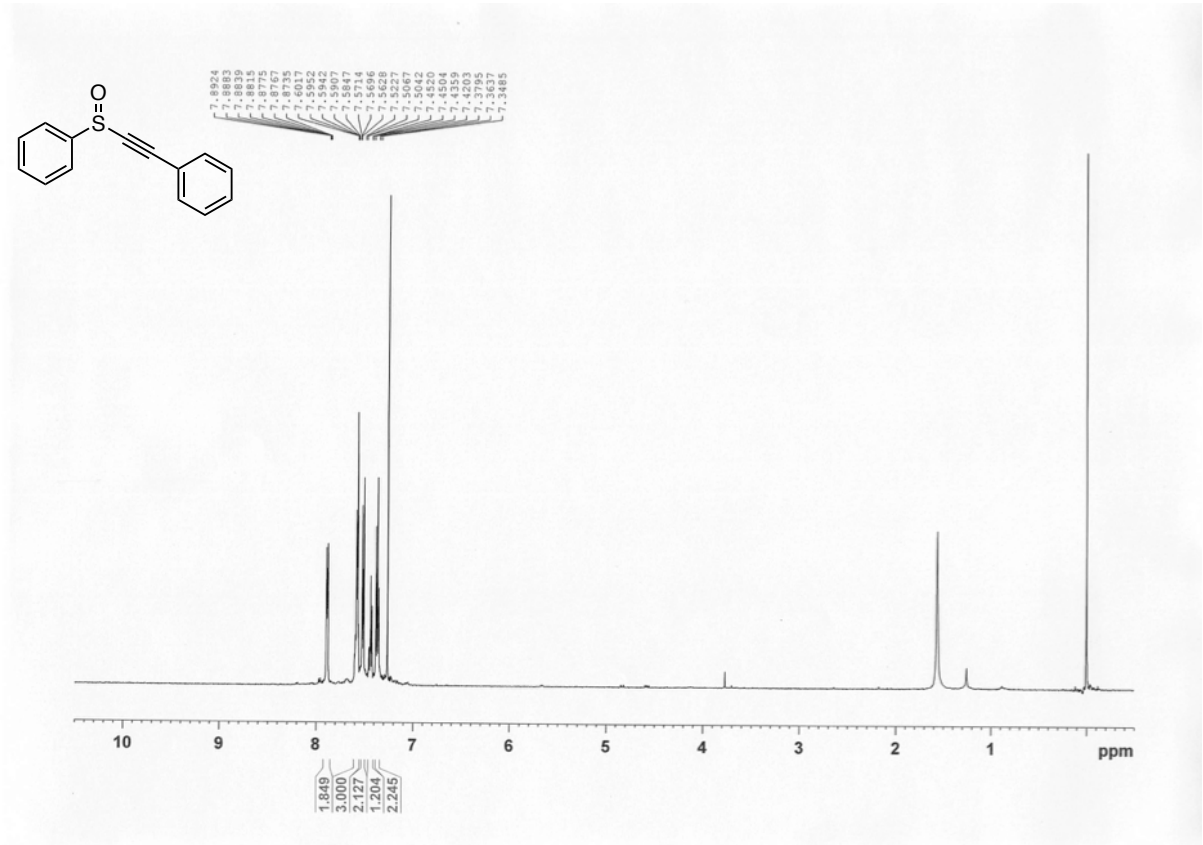




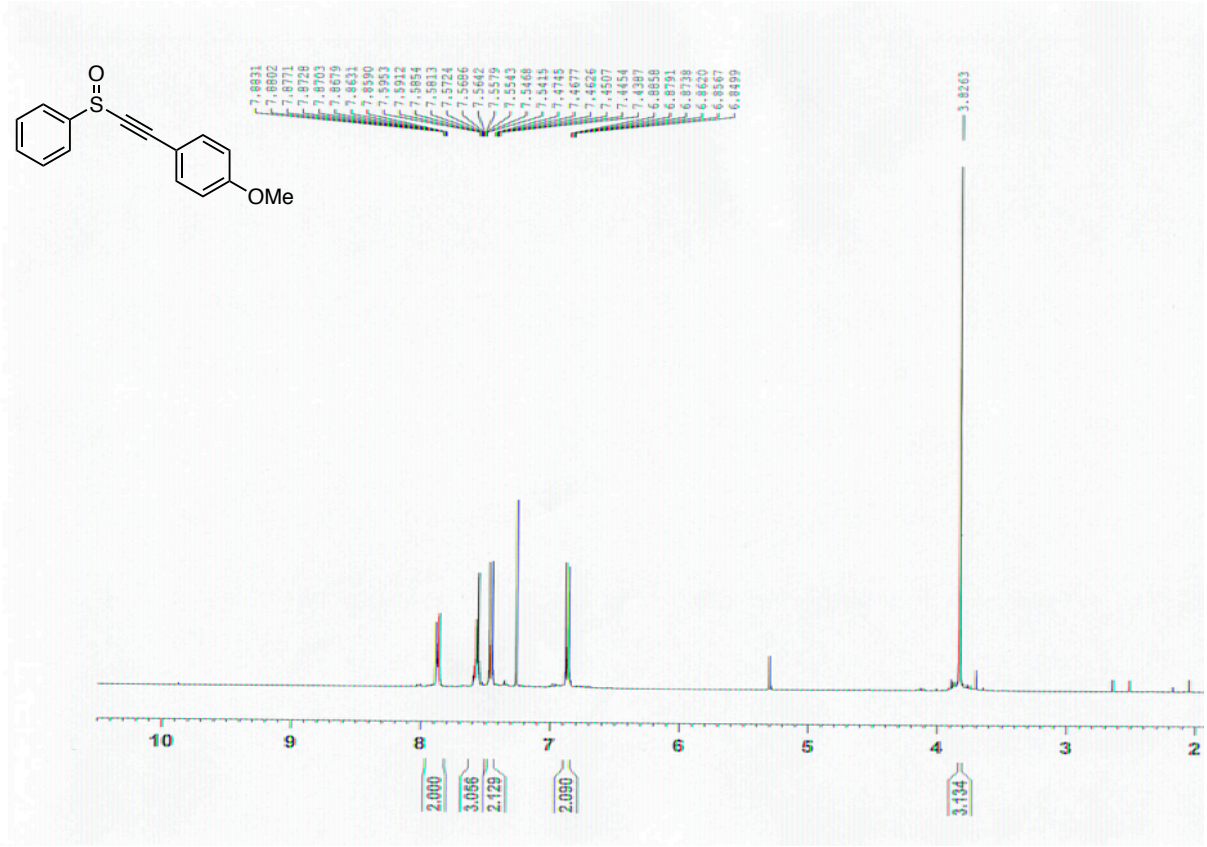
^{1}H NMR (400 MHz) spectra of phenyl 1-propynyl sulfoxide (**16a**) ($CDCl_3$)



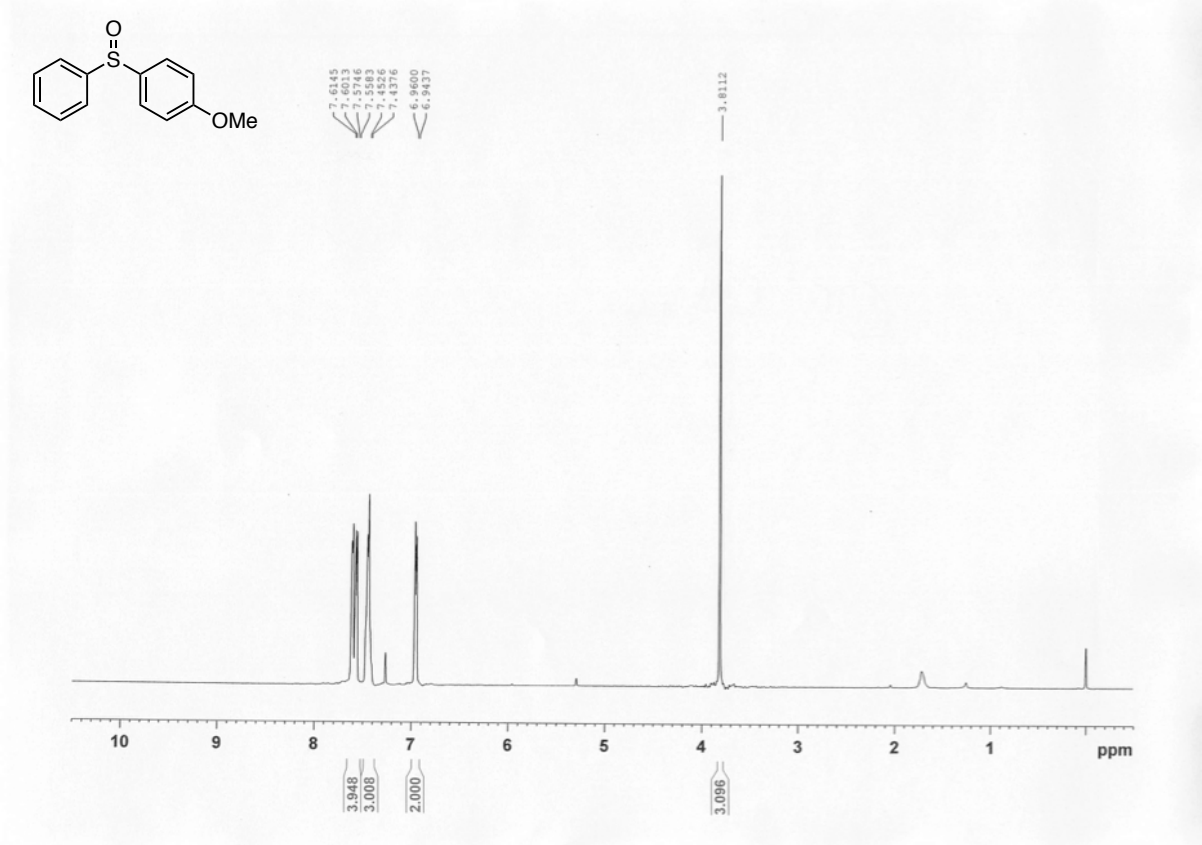
^{1}H NMR (400 MHz) spectra of phenyl phenylethynyl sulfoxide (**16b**) ($CDCl_3$)



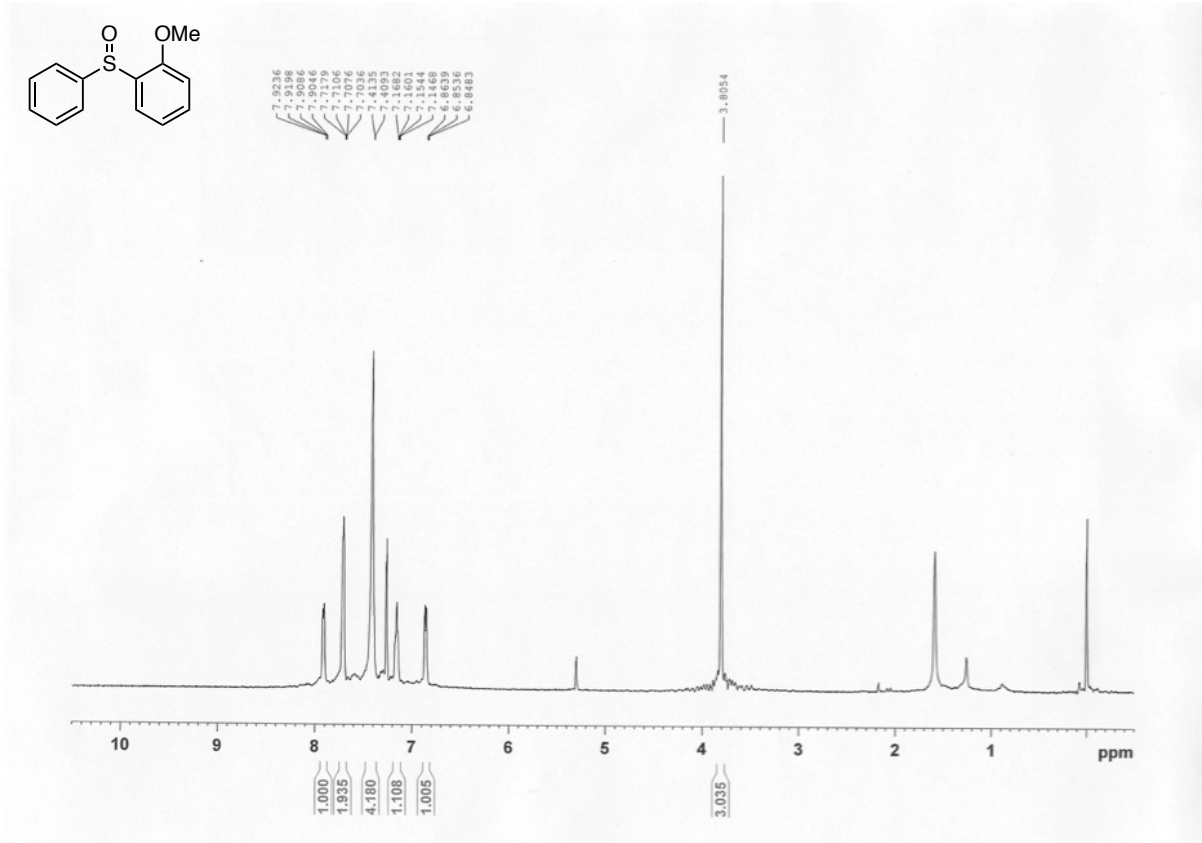
^{1}H NMR (400 MHz) spectra of 4-methoxyphenylethynyl phenyl sulfoxide (**16c**) ($CDCl_3$)



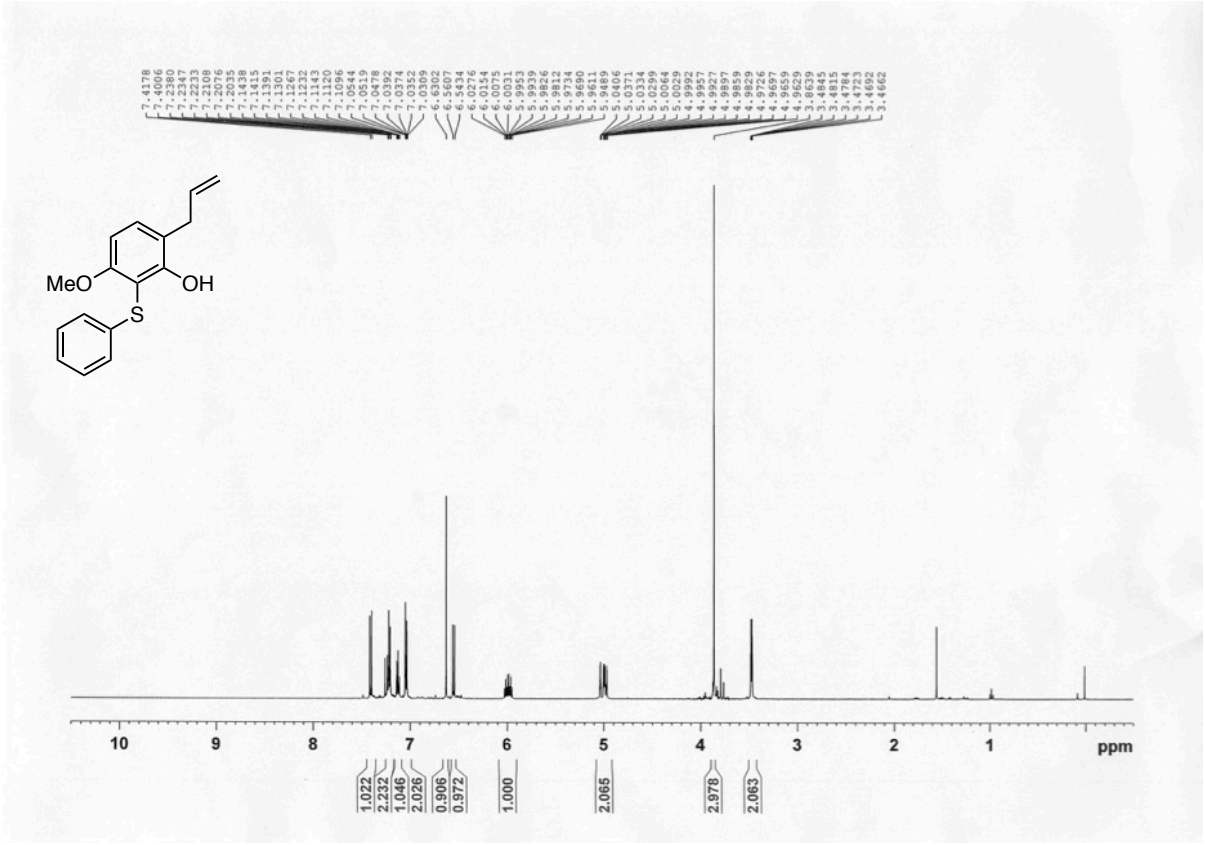
^{1}H NMR (400 MHz) spectra of 4-methoxyphenyl phenyl sulfoxide (**18**) ($CDCl_3$)

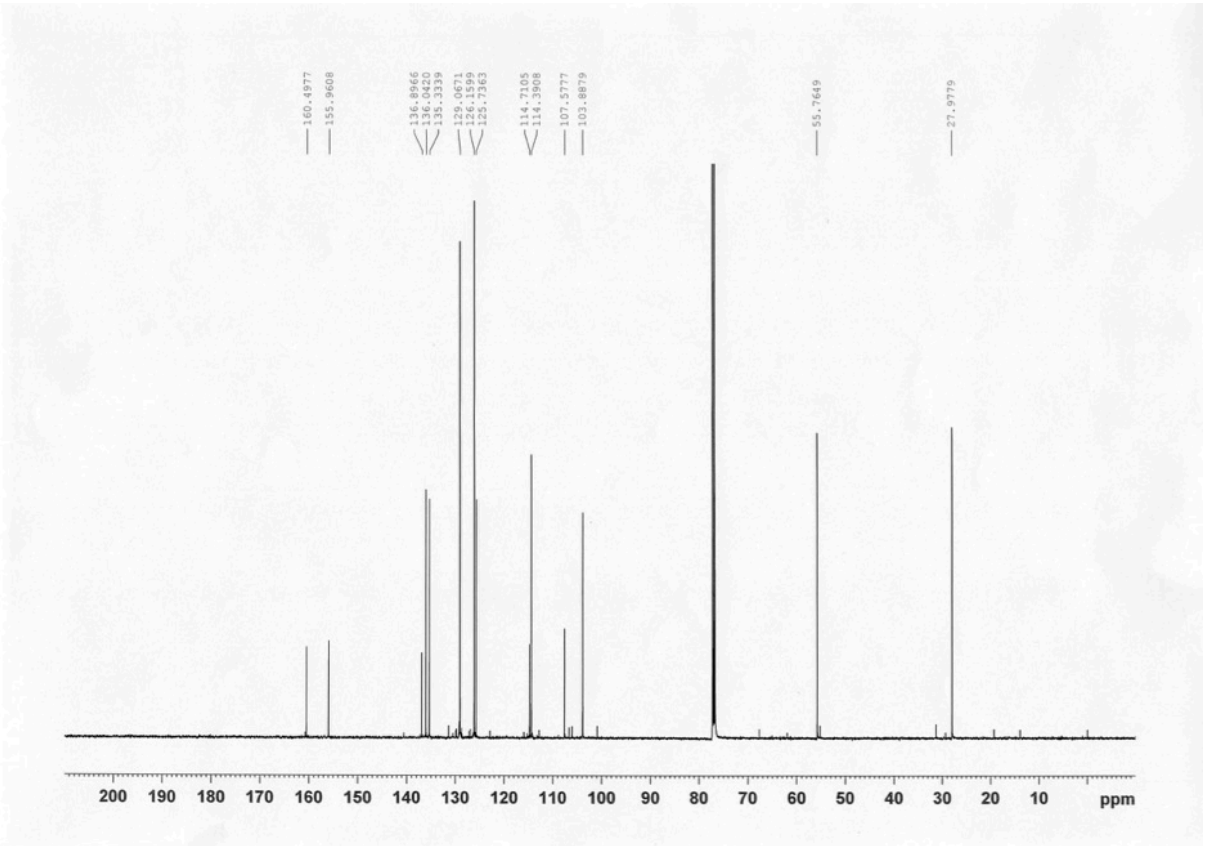


^{1}H NMR (400 MHz) spectra of 2-methoxyphenyl phenyl sulfoxide (**18'**) ($CDCl_3$)

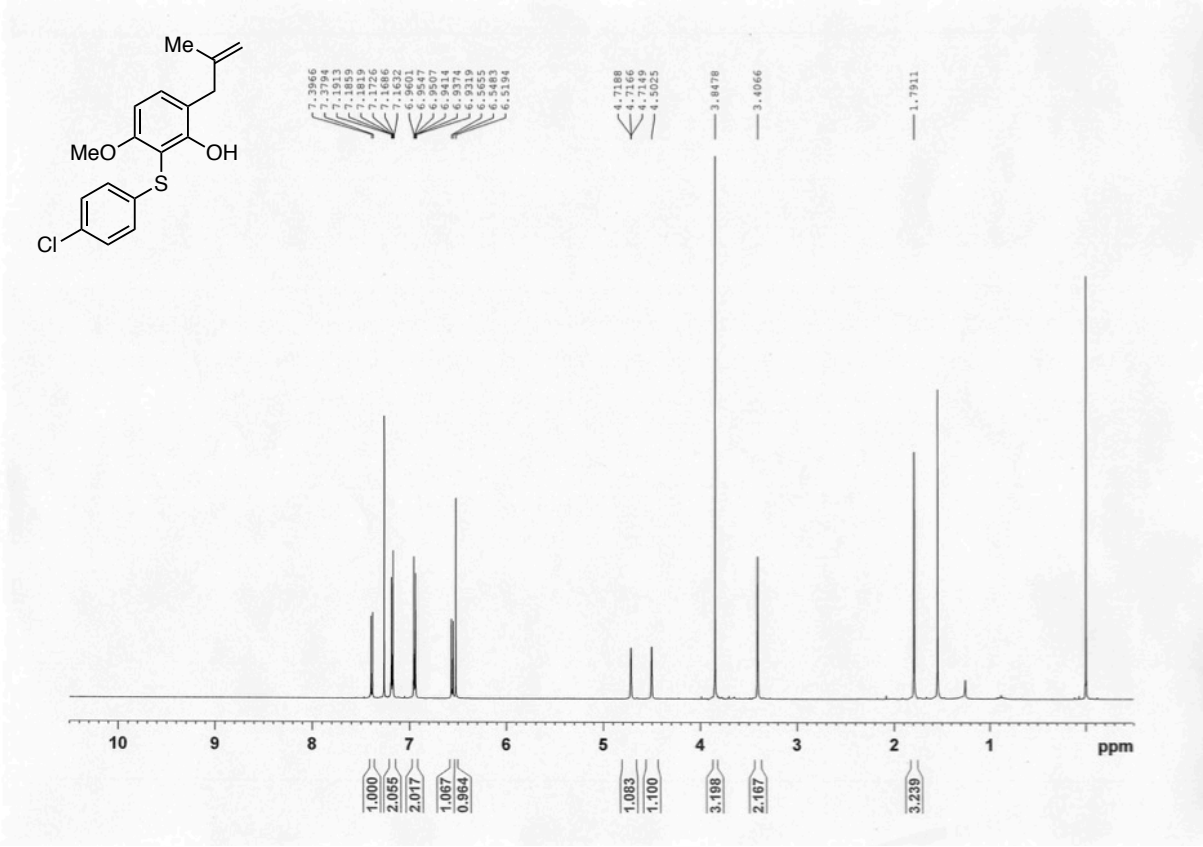


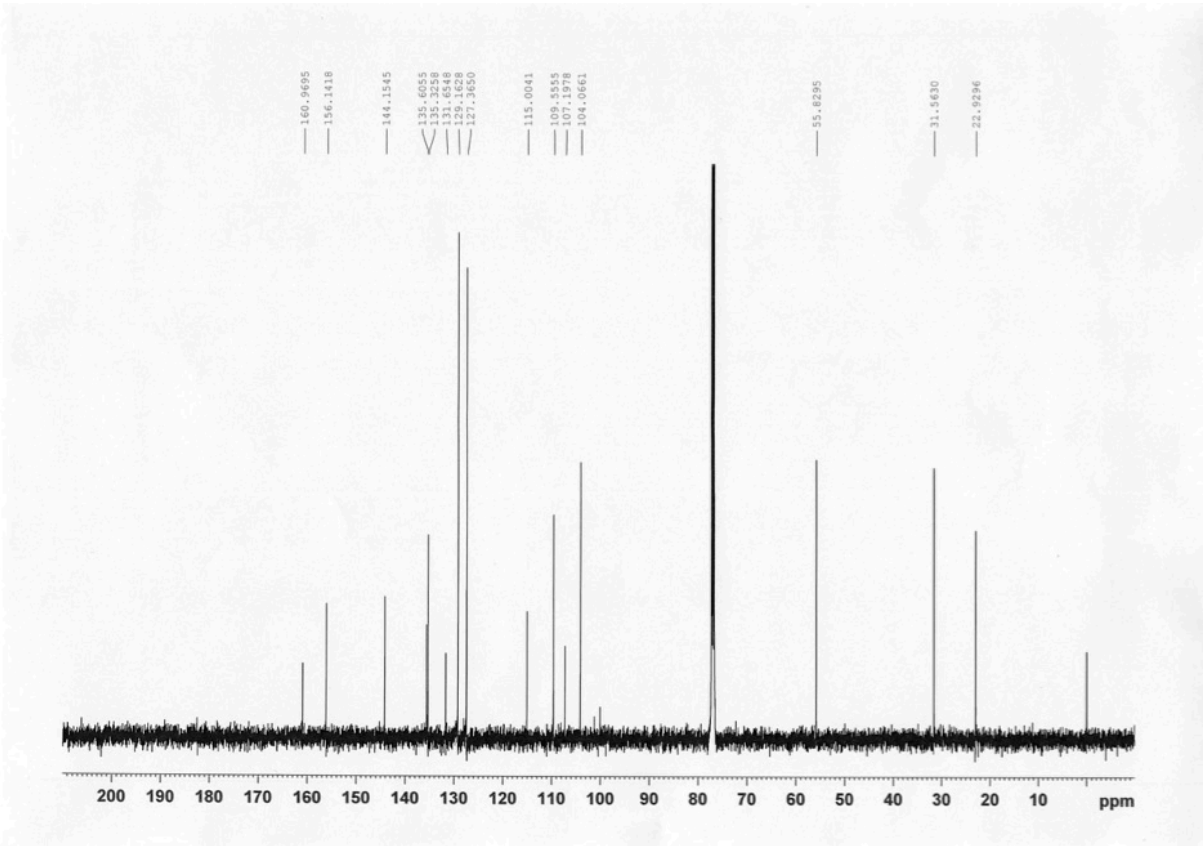
^{1}H NMR (500 MHz) and ^{13}C NMR (126 MHz) spectra of 6-allyl-3-methoxy-2-(phenylthio)phenol (**20a**) ($CDCl_3$)



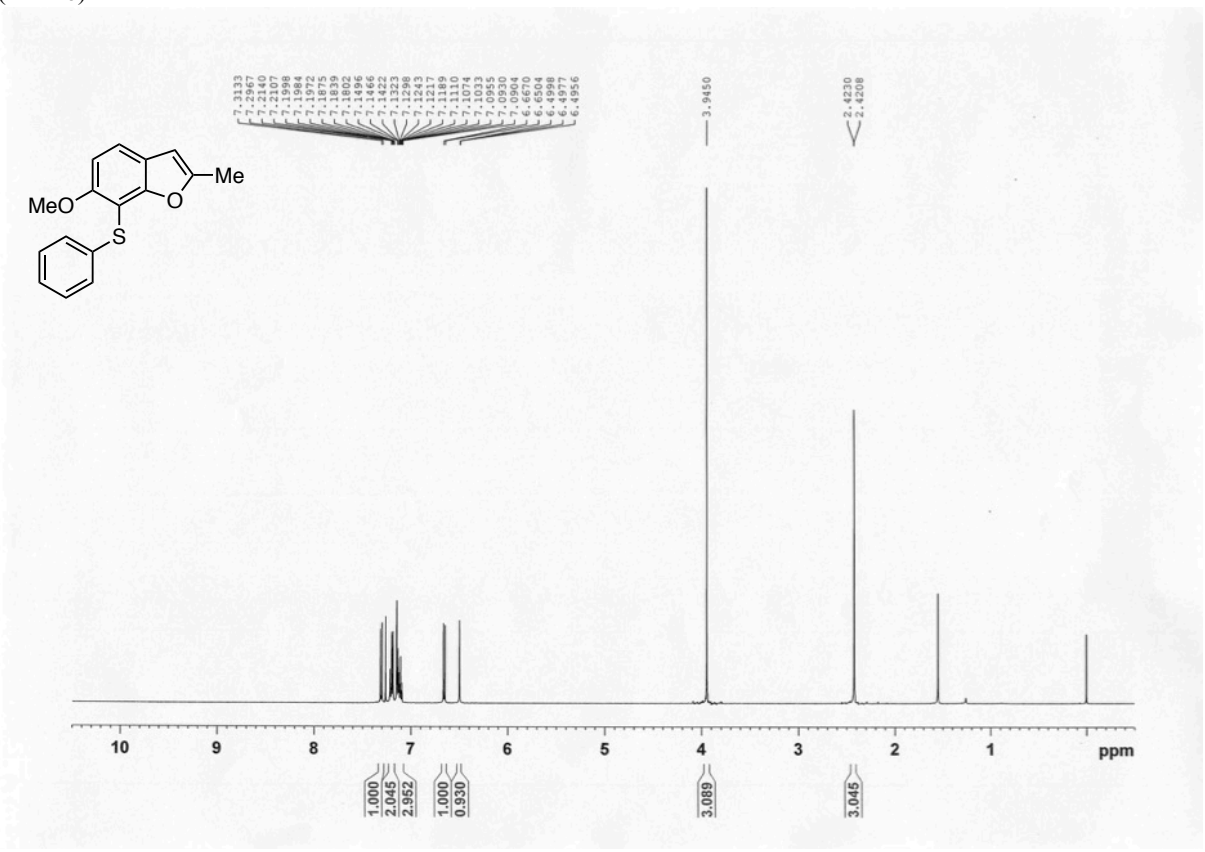


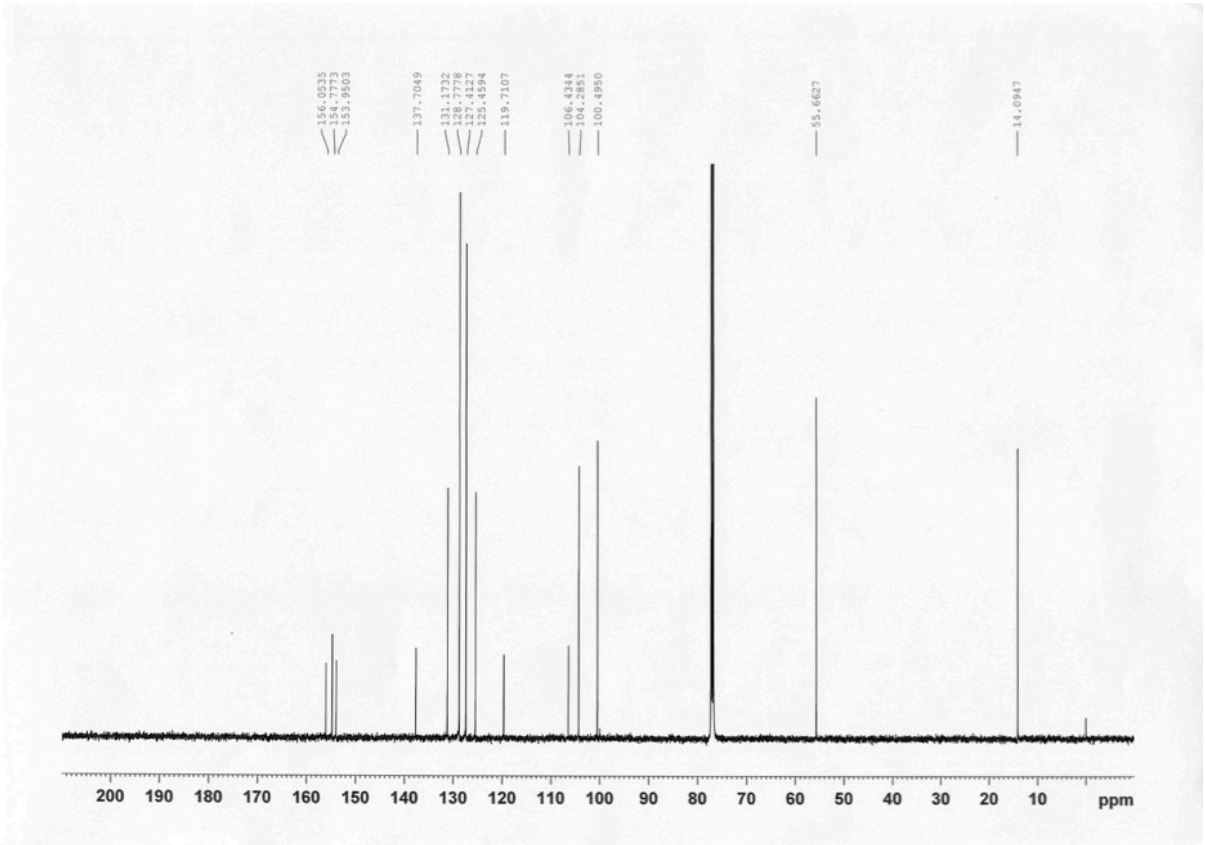
^{1}H NMR (500 MHz) and ^{13}C NMR (126 MHz) spectra of 2-((4-chlorophenyl)thio)-3-methoxy-6-(2-methylallyl)phenol (**20b**) ($CDCl_3$)





^{1}H NMR (500 MHz) and ^{13}C NMR (126 MHz) spectra of 6-methoxy-2-methyl-7-(phenylthio)benzo[*b*]furan (**21**) ($CDCl_3$)





^{1}H NMR (500 MHz) and ^{13}C NMR (126 MHz) spectra of 2-(2-bromoallyl)-3-((4-methoxyphenyl)thio)-5-triflyloxy-4-(trimethylsilyl)-1*H*-indole (**23**) ($CDCl_3$)